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THE HYDROLYSIS OF ACID AMIDES.

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The work[1] here reported was done two years ago in coöperation with the extensive investigations of Professor Acree and his coworkers on catalysis.[2] Though the conductivity side of the work still remains to be done, yet since I do not intend to continue the work from this point of view, it seems best to publish what has been done so far, so as to leave the way clear for the continuation of the work in other hands.

Acree and Nirdlinger,[3] working with acetamide and using hydrochloric acid as catalyst, found that the molecular reaction velocity varied considerably, both with the concentration of the amide and with that of the catalyst, the variation in both cases being in the direction, and of the magnitude, which was predicted from conductivity studies of the various solutions on the assumption which they made, that the reacting substance is a complex ion (or salt) formed by union of the hydrogen ion (or both ions) with the amide. This observation confirmed their belief in the analogy of the hydrolysis of acid amides to the formation of ethers and esters by the action of alkyl (acyl) halides on the salts of alcohols, phenols, urazoles,[4]

[1] This work was aided by a grant from the Carnegie Institution of Washington to S. F. Acree.

[2] THIS JOURNAL, **28**, 370; **37**, 71, 410; **38**, 258, 489, 746 **39**, 145, 226, 300. J. Am. Chem. Soc., **30**, 1755. Ber. d. chem. Ges., **41**, 3199.

[3] THIS JOURNAL, **38**, 489.

[4] Ber. d. chem. Ges., **41**, 3199. Also earlier and more recent papers.

etc., to esterification and the inversion of cane sugar as worked out by Bredig,[1] Goldschmidt, Kastle, and Acree and Johnson,[2] to the formation and hydrolysis of oximes, as shown by Lapworth and Barrett[3] and by Acree and Johnson[4] and Deshea,[5] and to the decomposition of imido esters as studied by Stieglitz.[6]

The present work was undertaken to test this theory more thoroughly by studying several amides at widely different concentrations both of amide and of catalyst. The amides used were benzamide and acetamide with barium hydroxide as catalyst. All of the work was done at 25°, so as to be more readily coördinated with existing conductivity data, as well as to facilitate the making of such additional conductivity measurements as might be required.

Materials.—The benzamide was recrystallized several times from water, once from dilute ammonia, once from alcohol, and finally from conductivity water. The acetamide was distilled several times and recrystallized from acetone. The barium hydroxide was recrystallized. Conductivity water of high purity was used in making and diluting all solutions on which measurements were to be made. Redistilled ammonia-free water was used in filling the distillation flasks.

Work with Benzamide.

Method of Work.—The reactions were carried on in Erlenmeyer flasks, of 120 cc. capacity, of "Nonsol" glass. Before use, they were heated for several days with dilute hydrochloric acid. The rubber stoppers used and the small tubes placed in the flasks were also well boiled out. The benzamide for an experiment was weighed into the flask, the proper amount of barium hydroxide solution and of pure water run in to make the desired strength of solution, the stopper inserted, and the flask gently shaken till all of the benzamide had gone into solu-

[1] Z. Elek. Chem., **9**, 118; **10**, 585, 586; **11**, 528.

[2] This Journal, **38**, 258. This article contains full references to many important articles on reaction mechanisms.

[3] J. Chem. Soc., **91**, 1133; **93**, 85.

[4] This Journal, **38**, 308; **39**, 300.

[5] Dissertation, Johns Hopkins University, 1909.

[6] Report International Congress of Arts and Sciences, St. Louis, **4**, 276. This Journal, **39**, 29, 176, 402, 437, 586, 719.

tion. The slight solubility of benzamide at 25° caused much trouble. In order to lessen the danger of loss of ammonia from the alkaline solution, a tube 18 by 60 mm., closed at one end, and containing enough dilute hydrochloric acid to absorb the ammonia likely to be given off during the reaction, was stood up in the flask before inserting the stopper. In order to prevent mixing of the solutions by crawling, the upper portion of the tube was coated with purified paraffin. The flask containing the reacting mixture was sunk to the neck in a water bath heated by electricity as described by Morse and Holland.[1] The temperature was kept constant to within about 0°.01. To stop the reaction, 5 cc. of a 5 normal magnesium chloride solution was run in.

Method of Analysis.[2]—The reaction mixture and the contents of the tube containing the acid were washed into a flask and distilled with steam for 70 minutes with magnesium hydroxide. The percentage of decomposition thus found was corrected for the amount of the remaining benzamide hydrolyzed during the distillation by subtracting 0.21 per cent. of $(100 - x)$ from x, where x is the percentage of decomposition found.[3]

Results.—Table I gives the results of experiments in which the concentration of the barium hydroxide was kept constant and that of the benzamide was varied from 0.015 to 0.060 normal. The time is given in days. The results are calculated by means of the usual formula for a reaction of the second order, A being the concentration of the barium hydroxide and B that of the benzamide. The upper half of the table gives the analytical data in percentage of decomposition found, and the lower half gives the values of K, the reaction velocity, calculated from these data. A few values of K which are out of harmony with the others in the series are given in parentheses and were not used in making the averages. In column 1, the amount of benzamide used was 0.1681 gram to 100 cc. of solution, while in the others

[1] This Journal, **41**, 92.
[2] *Ibid.*, **21**, 293.
[3] *Ibid.*, **41**, 486.

the amount of benzamide was 0.3363 gram, or 3 millimoles, to 100, 75 and 50 cc. of the barium hydroxide.

Table I.

A	0.3489	0.3489	0.3489	0.3489
B	0.015	0.030	0.040	0.060
A–B	0.3339	0.3189	0.3089	0.2889
A/B	23.26	11.63	8.722	5.815
	Percentage of Hydrolysis.			
1 day	33.96	32.75	32.49	31.53
2 days	55.51	53.55	52.77	51.06
3 days	70.30	68.20	66.58	66.09
4 days	79.33	78.60	77.03	73.98
6 days	91.24	.....	88.44	86.24
7 days	93.40	90.97	91.50	86.41
	Velocity Constants.			
1 day	1.171	1.155	(1.149)	1.118
2 days	1.177	1.132	1.113	1.082
3 days	1.182	1.134	1.111	1.108
4 days	(1.154)	1.154	1.116	1.048
6 days	1.181	.....	1.094	1.025
7 days	1.145	1.041	1.099	(0.907)
Average	1.171	1.118	1.107	1.075

The results show that the reaction proceeds regularly till at least 90 per cent. of the benzamide is used up.

Table II gives the results of experiments in which the concentration of the amide was kept constant and that of the barium hydroxide was varied. The amount of benzamide was 0.3363 gram and the volume was 75 cc. The values in column 1 are taken from column 3 of Table I.

Table II.

A	0.3489	0.30	0.20	0.10
B	0.040	0.40	0.04	0.04
A–B	0.3089	0.25	0.16	0.06
A/B	8.722	7.50	5.00	2.50
	Percentage of Hydrolysis.			
1 day	32.49	27.35	.....	.....
2 days	52.77	.....	30.62	14.97
3 days	66.58	60.31	42.60	22.22
4 days	77.03	71.02	51.31	27.43

Velocity Constants.

1 day	(1.149)	1.086	.....	.....
2 days	1.113	.....	0.945	0.837
3 days	1.111	1.077	0.970	0.878
4 days	1.116	1.097	0.955	0.852
Average	1.118	1.087	0.963	0.865

Acetamide.

The following work with acetamide was intended to parallel that with benzamide in a general way. Owing to the greater reactivity of acetamide, the time periods are much shorter and hours take the place of days in the table. On account of its greater solubility considerably greater concentrations of amide could be used. The concentrations of the barium hydroxide were the same, with the addition of one 0.05 normal. The results are not satisfactory though much work was put upon them. The small molecular weight of acetamide makes rather accurate weighings necessary, but acetamide is very hygroscopic and gains rapidly in weight during the weighing, the gain varying according to the weather. In some of the experiments a 0.3 normal stock solution was made up and 10 cc. of this measured into each flask. However, it was found that such a solution, even when made up with conductivity water, is hydrolyzed appreciably in a day or two, so that fresh solutions had to be prepared for each day's work. The acetamide was crystallized from acetone and was kept in a desiccator all the time. It must have occluded some of the solvent or have failed to dry in the desiccator since equal weighed samples gave irregular amounts of ammonia on distillation with sodium hydroxide. A further cause of uncertainty in the results is that the amount of acetamide decomposed by boiling with magnesium hydroxide is considerable, amounting to 0.4 per cent. on the average, but seeming to be somewhat irregular as judged from a number of blank experiments.

In Table III are given results of experiments with barium hydroxide of constant concentration and acetamide of six concentrations from 0.03 up to 0.30 normal, that is, with 0.1772 gram of acetamide in 100, 75, 50, 25, 15 and 10 cc.

of the barium hydroxide solution. The amide was weighed into each of the flasks or tubes. For the three larger volumes, flasks were used exactly as described for benzamide, but for the smaller volumes, i. e., 25, 15 and 10 cc., test tubes were employed. These had previously been drawn down to a neck and were sealed off immediately after putting in the solution.

In the analysis of the reaction mixtures the ammonia was first determined by distillation with magnesium hydroxide in the usual way and then, after putting on another receiver, excess of strong sodium hydroxide solution was run in and the distillation continued for an hour longer. This decomposed the acetamide present and drove over most of the resulting ammonia. After an hour's distillation with the caustic soda, the receiver was removed and an empty flask put in its place and the distillation continued for one hour more. The ammonia thus obtained was usually equivalent to between 0.04 and 0.10 cc. of tenth-normal acid. Since 3 millimoles of acetamide was used, which should give ammonia equivalent to 30 cc. of tenth-normal acid, the three amounts of ammonia found should, when added together, equal this amount. The standard acid used was of such strength that the amount neutralized should have been 30.06 instead of 30 cc.

In the first part of the table are given the concentrations, etc., in the next part the amounts of standard acid neutralized in the three distillations of each sample, then the percentage of decomposition corrected for the amount of amide decomposed by the magnesium hydroxide, and finally, in the lower portion, the velocity constants calculated from these percentages. It will be noted that the amounts of acid neutralized seldom add up to 30.06 cc., the calculated amount. This is likely due to several causes: the amide may have contained irregular amounts of water as mentioned above, or some ammonia may have been lost either from the flasks in the long-time periods or during the transfer of the reaction mixtures to the distilling flasks. To avoid leakage the stoppers were inserted as tightly as practicable in the reaction flasks, and to avoid loss of ammonia during the transfer, the reaction

mixtures were made as nearly neutral as possible immediately after stopping the reaction. Besides, there may have been some loss during distillation, and there are always errors in the titration of large volumes of liquids and these, of course, added in some cases and cancelled in others. The percentage of decomposition is calculated in each case from the total ammonia actually found rather than from the amount calculated.

A is the concentration of the barium hydroxide and *B* that of the acetamide. The time is given in hours.

Table III.—Acetamide.

A	0.3489	0.3489	0.3489	0.3489	0.3489	0.3489
B	0.03	0.04	0.06	0.12	0.20	0.30
A–B	0.3189	0.3089	0.2889	0.2289	0.1489	0.0489
A/B	11.67	8.722	5.815	2.907	1.744	1.163
Volume	100	75	50	25	15	10

Titrations.

5 hours	6.79	6.74	6.66	6.52	6.22	6.01
	22.95	22.99	23.27	23.36	23.74	23.96
	0.09	0.11	0.04	0.06	0.01	0.04
	29.83	29.84	29.97	29.94	29.97	30 01
15 hours	15.48	15.30	15.17	14.66	13.61	12.82
	14.30	14.36	14.52	15.25	16.31	17.11
	0.10	0.10	0.05	0.05	0.04	0.03
	29.88	29.76	29.74	29.96	29.96	29.96
20 hours	19.66	19.27	18.92	18.26	17.12	15.67
	10.30	10.43	10.72	11.57	12.73	14.18
	0.10	0.09	0.02	0.02	0.02	0.04
	30.06	29.79	29.66	29.85	29.87	29.89
40 hours	25.39	25.23	25.27	24.35	22.67	20.70
	4.18	4.22	4.52	5.57	7.14	9.14
	0.09	0.09	0.05	0.07	0.00	0.03
	29.66	29.34	29.84	29.99	29.81	29.87

70 hours	28.73	28.52	.....	27.69	26.28	23.80
	1.07	1.25	.....	1.97	3.39	5.67
	0.05	0.09	.....	0.02	0.04	0.04
	29.85	29.86	.....	29.68	29.71	29.51

Corrected Percentages of Hydrolysis.

5 hours	22.45	22.28	21.91	21.46	20.43	19.71
15 hours	51.61	51.21	50.81	48.73	45.21	42.56
20 hours	65.32	64.41	63.71	61.08	57.22	52.44
40 hours	85.57	85.56	84.65	81.15	76.00	69.24
70 hours	96.23	95.49	.....	93.27	88.40	80.58

Velocity Constants.

5 hours	0.1472	0.1465	0.1446	0.1440	0.1405	0.1383
15 hours	0.1422	0.1418	0.1426	0.1411	0.1359	0.1347
20 hours	0.1570	0.1548	0.1553	0.1546	0.1525	0.1469
40 hours	0.1458	0.1483	0.1486	0.1465	0.1444	0.1402
70 hours	0.1430	0.1380	[0.1420]	0.1442	0.1381	0.1272
Average	0.1470	0.1459	0.1471	0.1461	0.1427	0.1374

The value in brackets was supplied from adjacent values so as to balance the different time periods in the general averages. In these experiments, as in the ones that follow, all the samples for the same time period were in the bath together so that any fluctuation of the temperature affected all alike. In the 20-hour experiments the temperature was too high for a part of the time. The purpose of the experiments was to find the influence of the concentration of the amide on the velocity, and this influence is broguht out in this table in spite of its imperfections. The work was, however, repeated and somewhat enlarged and the results are given in Table IV, which follows. The fact that the total ammonia found in the titrations is larger is partly due to expansion of the standard solutions in warmer weather. The concentration of amide varied, the base remaining constant.

Table IV.—Original Concentrations.

A	0.3489	0.3489	0.3489	0.3489	0.3489	0.3489
B	0.03	0.04	0.06	0.12	0.20	0.30
A–B	0.3189	0.3089	0.2889	0.2289	0.1489	0.0489
A/B	11.67	8.722	5.815	2.907	1.744	1.163
Volume	100	75	50	25	15	10

Titrations.

2.5 hours	3.59	3.56	3.64	3.55	3.22	3.22
	25.94	26.17	26.21	26.37	26 33	26.10
	0.07	0.11	0.05	0.04	0.02	0.06
	29.60	29.34	29.90	29.96	29.56	29.38
5 hours	6.90	6.43	6.60	6.45	6.33	5.75
	22.96	22.41	23.27	23.40	23.44	23.62
	0.18	0.17	0.08	0.05	0.04	0.05
	30.04	29.01	29.95	29.90	29.82	29.42
10 hours	11.74	11.55	11.51	11.14	.....	10.01
	18.31	18.48	18.44	18.98	.....	20.01
	0.09	0.09	0.08	0.06	.....	0.02
	30.14	30.12	30.03	30.20	.....	30.04
15 hours	15.61	.....	15.38	14.74	13.83	12.31
	14.25	14.45	14.68	15.30	15.99	16.99
	0.09	0.09	0.06	0.06	0.02	0.04
	29.95	.....	30.12	30.10	29.84	29.34
20 hours	18.53	18.32	18.35	17.43	16.49	15.12
	11.39	11.41	11.74	12.57	13.59	14.75
	0.12	0.14	0.06	0.08	0.05	0.03
	30.04	29.87	30.15	30.08	30.13	29.90
30 hours	22.78	22.71	22.36	21.34	19.93	18.20
	7.12	7.36	7.64	8.79	10.03	11.73
	0.12	0.10	0.06	0.04	0.06	0.04
	30.02	30.17	30.06	30.17	30.02	29.97
50 hours	27.11	26.88	26.62	25.61	24.18	.....
	2.91	3.01	3.32	4.24	5.83	
	0.09	0.10	0.05	0.04	0.05	
	30.11	29.99	29.99	29.89	30.06	.....

70 hours	28.73	28.56	28.41	27.71	26.28	24.03
	1.29	1.29	1.46	2.25	3.61	5.76
	0.06	0.08	0.02	0.05	0.04	0.05
	30.08	29.93	29.89	30.01	29.93	29.84

Corrected Percentages of Hydrolysis.

2.5 hours	11.84	11.61	11.85	11.53	10.57	10.64
5 hours	22.69	21.88	21.76	21.29	20.95	19.25
10 hours	38.88	38.16	38.04	36.69	.....	33.09
15 hours	51.95	.....	50.88	48.78	46.16	41.76
20 hours	61.55	61.19	60.71	57.80	54.56	50.39
30 hours	75.77	75.18	74.29	70.63	66.27	60.59
50 hours	90.01	89.59	88.72	85.63	80.37	.....
70 hours	95.50	95.40	95.03	92.32	87.76	80.53

Velocity Constants.

							Average.
2.5 hrs.	0.1440	0.1424	(0.1461)	0.1433	0.1425	0.1355	0.1415
5 hrs.	0.1437	0.1410	0.1434	0.1427	0.1437	0.1341	0.1419
10 hrs.	0.1437	0.1411	0.1427	0.1407	[0.1414]	0.1371	0.1411
15 hrs.	0.1437	0.1428	0.1429	0.1413	0.1404	(0.1305)	0.1403
20 hrs.	0.1413	0.1414	0.1426	0.1409	0.1372	0.1360	0.1401
30 hrs.	0.1411	0.1407	0.1409	0.1380	0.1372	0.1328	0.1385
50 hrs.	0.1395	0.1394	0.1398	0.1391	0.1365	.....	0.1389
70 hrs.	0.1354	0.1370	0.1396	0.1362	0.1350	0.1333	0.1360
Average,	0.1416	0.1407	0.1417	0.1403	0.1392	0.1348	.....

The value in brackets is supplied by interpolation.

The next question taken up was the effect of changes in the concentration of the barium hydroxide and of the presence of neutral salts on the velocity of the reaction, the concentration of the acetamide being kept constant. The results of these experiments are given in Tables V and VI, of which V is merely preliminary. The volume of the reaction mixture was in all cases 75 cc. In Table VI, the values for the 0.3489 N base are taken from Table IV for the same concentration of the amide. For the experiments with addition of barium chloride, the barium salt as well as the amide were weighed into the flask for each experiment, but for the other experiments, 10 cc. of a 0.3 normal solution of the amide was measured out each time and the calculated amount of the strong barium-

hydroxide solution and of conductivity water added to make the required strength of solution. The acetamide solution was made up just before using. The six samples for the same time period were always in the bath at the same time so that any variation in temperature could not affect the relative values. Since all the samples in a set contained the same original amount of amide, only one distillation was made in the analysis of the reaction mixture. The results for the 0.3489 normal base and for this plus 1 normal barium chloride are not strictly comparable since in these the amide was weighed for each experiment instead of being measured out from a stock solution, and in the former the percentage was calculated from the total ammonia actually found rather than from the weight of the amide.

Table V.

Original Concentrations.

A	0.30	0.20	0.10
B	0.04	0.04	0.04
A–B	0.26	0.16	0.06
A/B	7.5	5.0	2.5

Percentages of Hydrolysis, Corrected.

5 hours	19.33	13.05	6.50
20 hours	55.17	40.99	22.97
72 hours	93.75	83.38	57.65

Velocity Constants.

5 hours	0.1452	0.1417	0.1362
20 hours	0.1396	0.1381	0.1372
72 hours	0.1410	0.1400	0.1382
Average	0.1419	0.1399	0.1372

Table VI.

Original Concentrations, etc.

A	0.3489	0.3489 $+BaCl_2$	0.30	0.30 $+Ba(C_2H_3O_2)_2$	0.20	0.10	0.05
B	0.04	0.04	0.04	0.04	0.04	0.04	0.04
A–B	0.3089	0.3089	0.26	0.26	0.16	0.06	0.01
A/B	8.722	8.722	7.50	7.50	5.00	2.50	1.25

Percentages of Hydrolysis, Corrected.

2.5 hrs.	11.64	11.55	9.25	10.42	7.07	3.50	1.73
5 hrs.	22.88	21.57	17.84	19.50	12.59	6.67	3.16
10 hrs.	38.16	37.53	22.31	34.00	23.75	12.71	6.66
15 hrs.	.....	50.73	44.56	46.40	33.24	18.57	9.70
20 hrs.	61.19	61.07	53.78	55.99	41.43	23.42	12.70
30 hrs.	75.18	71.41	67.93	70.61	54.38	32.10	17.52
50 hrs.	89.59	88.40	82.99	85.94	72.12	46.32	26.69
70 hrs.	95.40	94.07	91.09	92.40	81.40	56.04	33.50

Velocity Constants.

2.5 hrs.	0.1424	0.1416	0.1385	0.1477	0.1476	0.1435	0.1416
5 hrs.	0.1410	0.1412	0.1327	0.1419	(0.1354)	0.1372	(0.1304)
10 hrs.	0.1411	0.1380	0.1331	0.1420	0.1390	0.1396	0.1417
15 hrs.	0.1428	0.1398	0.1355	0.1436	0.1400	0.1422	0.1417
20 hrs.	0.1414	0.1410	0.1341	0.1429	0.1401	0.1403	0.1434
30 hrs.	0.1407	(0.1259)	0.1336	0.1444	0.1395	0.1387	0.1387
50 hrs.	0.1394	(0.1325)	(0.1273)	0.1415	0.1402	0.1391	0.1385
70 hrs.	(0.1370)	(0.1254)	(0.1258)	(0.1343)	(0.1343)	(0.1352)	0.1371
Aver.	0.1415	0.1400	0.1338	0.1427	0.1398	0.1400	0.1401

In making up the averages, the values in parentheses are left out as being out of harmony with adjacent values, as are also those for the 2.5-hour time period. In these short-period experiments, particularly with the lower concentrations of base, the amount of ammonia found is very small and the correction for acetamide decomposed during the distillation with magnesium hydroxide is comparatively large, and the results are therefore uncertain. In the very long time periods there is greater danger of loss of ammonia, disturbing influences due to the change of the medium, etc., have a greater opportunity to affect the results, and the reaction being so nearly complete, the change per hour is extremely slow and consequently unavoidable analytical errors influence the results unduly. In the higher concentrations, at the end of 70 hours the reaction is progressing at the rate of only 0.2 per cent. per hour. For this reason, values for time periods of over 30 hours were not used in making up the averages for the highest concentration.

Hydrolysis of Acetamide in Pure Water.

One of the solutions, which, after standing several days, showed slight hydrolysis, was examined microscopically and appeared to contain bacteria, but of what kind they were or whether they were in any way connected with the hydrolysis was not determined. Two of these 0.3 normal solutions of acetamide stood about 18 months in clean glass-stoppered bottles without being opened in the interval. On analysis, one showed 23.2 and the other 55.2 per cent. hydrolysis.

DISCUSSION OF RESULTS.

Change of Velocity with Change of Concentration of the Amide.

In Table VII, the average velocities for benzamide are taken from Table I and those for acetamide from Table IV, the latter being multiplied by 24 to change velocity per hour into velocity per day.

Table VII.

Concentration of amide	0.015	0.03	0.04	0.06	0.12	0.20	0.30
Dilution	66.67	33.33	25.00	16.67	6.67	5.00	3.33
Benzamide	1.171	1.118	1.107	1.076	.....	.....	.....
Acetamide	.....	3.399	3.382	3.389	3.367	3.336	3.235

The same results are represented graphically below (Fig. I).

It appears that with benzamide, the velocity of the reaction decreases as the concentration of the amide increases, while for acetamide the velocity remains constant within the limits of experimental error till comparatively high concentrations are reached and then there is a decrease of the velocity with further increase of the concentration. The conduct of the benzamide is what was to have been expected according to the hypothesis of Acree and Nirdlinger.

In the work of Remsen and Reid,[1] done twelve years ago, on the hydrolysis of acid amides for the purpose of obtaining evidence bearing on the "hindrance" theory of Victor Meyer, a few amides were studied at concentrations of 0.04 and 0.02 normal relative to the amide. The results[2] in Table VIII

[1] THIS JOURNAL, **21**, 284–348, and **24**, 397–424.

[2] *Ibid.*, **21**, 340, 341.

are taken from the work then published, each of the constants quoted being the average of a series.

Table VIII.—With Hydrochloric Acid at 100°.

Concentration of amide	0.02	0.04
p-Nitrobenzamide	0.0256	0.0236
p-Chlorbenzamide	0.0200	0.0179
m-Brombenzamide	0.0210	0.0184
p-Brombenzamide	0.0180	0.0145
With Barium Hydroxide at 100°.		
m-Brombenzamide	0.283	0.273

In the case of the *m*-brombenzamide the hydrolysis went on with barium hydroxide 3.7 per cent. faster in the 0.02 normal than in the 0.04 normal solution. In the present

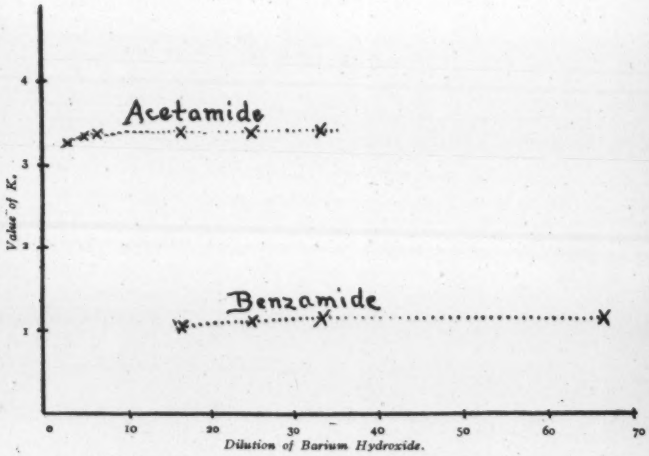


Fig. I.

work it is found that benzamide is hydrolyzed by the same base 3.9 per cent. faster in a 0.03 normal than in a 0.06 normal solution. When acid was used as catalyst, a greater differ-

ence, amounting to about 10 per cent., was found at the two concentrations of the amide. This agrees well with the greater differences found by Acree and Nirdlinger when hydrochloric acid was used as catalyst. In all cases the velocity of the reaction increases as the concentration of the amide diminishes, as is demanded by the theory, since the smaller the actual amount of amide present, which is a very weak base, the greater proportion of that small amount which will combine with the catalyst ion to form the reactive complex ion.

Effect of Neutral Salts.

Turning to columns 1 and 2 of Table VI, we find the average velocity, when the solution is 1 normal with respect to barium chloride, is 0.1400 as compared with an average of 0.1416 when no neutral salt is added. This difference, of about one per cent., though small compared with the experimental error, yet appears to be real since the difference is in the same direction in all eight of the experiments. Remsen and Reid[1] found that sodium sulphate diminished the rate of hydrolysis of the nitrobenzamides by caustic soda. Comparing the velocities found in column 3 of Table VII with those found in column 4 we find that the addition of one-half mole of barium acetate lowers the reaction velocity about six per cent. It is surprising that the acetate should be so much more effective than the chloride. The retarding influence of the barium acetate formed during the reaction accounts, in part, for the low values found for long-time periods.

Change of Velocity with Change of Concentration of Base.

The range of concentrations, from 0.35 to 0.05 normal, is not as great as is desirable, but was limited by the comparatively small solubility of the barium hydroxide. The average velocities from Tables II and VI are brought together in Table IX, those for acetamide being multiplied by 24 to make them comparable as to time periods with those for benzamide.

[1] This Journal, **21**, 342.

Table IX.

Concentration of base	0.3489	0.30	0.20	0.10	0.05
Dilution of base	2.89	3.33	5.00	10.00	20.00
Benzamide	1.118	1.087	0.963	0.865	.....
Acetamide	3.40	3.42	3.35	3.36	3.38

These are shown graphically in the diagram (Fig. II). With

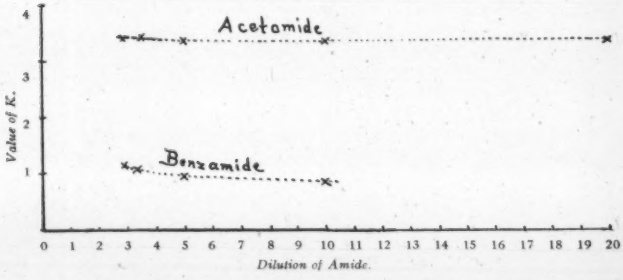


Fig. II.

benzamide, the velocity goes down steadily and regularly with increase of the dilution of the base. In the case of acetamide the change is much less and the uncertainty of the data is greater so that a conclusion is difficult, but the drift is in the same direction as with benzamide.

The Temperature Coefficient of the Reaction.

In previous work,[1] I found the velocity for 0.04 normal benzamide with 0.1 normal barium hydroxide at 100° to be 0.0944. In this the time was measured in minutes so that this must be multiplied by 1440 to change it to days. This gives 136.2, which, divided by 0.865, the velocity now found for the same concentrations of amide and base at 25°, shows that the reaction proceeds 157.5 times as fast at 100° as at 25°. This gives a temperature coefficient of 1.963 for each 10°.

My chief interest has been in making the measurements

[1] THIS JOURNAL, **24**, 419.

and in a study of the facts: the theoretical side of the problem will be discussed in later papers by Professor Acree and his collaborators when more data have been accumulated.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
Dec. 16, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXVIII.—THE TRANSFORMATION OF ALLYLPHTHALIMIDE INTO PROPENYLPHTHALIMIDE.

BY TREAT B. JOHNSON AND D. BREESE JONES.

Nomenclature.—New data are presented in this paper which contribute to our knowedge of the chemistry of propylene compounds, and in order to avoid confusion in distinguishing substitution products of this unsaturated hydrocarbon the terms *allyl* and *propenyl* are assigned to the groupings I and II, respectively. It seemed desirable to call attention to this

$$\underset{\text{I.}}{-CH_2.CH:CH_2} \qquad \underset{\text{II.}}{-CH:CH.CH_3} \qquad \underset{\text{III.}}{CH_2:C.CH_3}$$

distinction of terms because of the many irregularities in the nomenclature of allyl and propenyl compounds which appear in the chemical literature. Attention has previously been called to this confusion of terms in a paper by August Klages.[1]

Seitz, in a paper entitled "Zur Kenntniss halogenhaltiger Amine der Fettreihe,"[2] showed that β-brompropylphthalimide, IV, reacts smoothly, in alcohol, with potassium thiocyanate and potassium sulphydrate, with direct replacement of the bromine atom, giving β-thiocyanpropylphthalimide, V, and β-mercaptopropylphthalimide, VI, respectively. He also

$$\underset{\text{IV.}}{C_6H_4(CO)_2N.CH_2.CHBr.CH_3} \begin{cases} \xrightarrow{KSCN} \underset{\text{V.}}{C_6H_4(CO)_2NCH_2CH(SCN)CH_3} \\ \xrightarrow{KSH} \underset{\text{VI.}}{C_6H_4(CO)_2NCH_2CH(SH)CH_3}. \end{cases}$$

examined the behavior of this bromide towards aniline and observed that they reacted at 150°, in a unique manner, with an interchange of the phenyl and bromisopropyl radicals,

[1] Ber. d. chem. Ges., **35**, 2247 (1902).
[2] *Ibid.*, **24**, 2627 (1891).

giving phenylphthalimide, VII, and β-brompropylamine, VIII. A part of the bromide, however, reacted normally, giving as a secondary product of the reaction β-anilinopropylphthalimide, IX. These changes are expressed by the following scheme:

$$C_6H_4(CO)_2N.CH_2CHBrCH_3 +$$

$$C_6H_5NH_2 \rightarrow \begin{cases} C_6H_4(CO)_2N.C_6H_5 \text{ (VII.)} + NH_2.CH_2CH.BrCH_3 \text{ (VIII.)} \\ C_6H_4(CO)_2NCH_2CH(NHC_6H_5)CH_3 \text{ (IX.)} \end{cases}$$

Bartholdy[1] later investigated the action of alkali on this bromide and observed that the bromine atom could be replaced by the hydroxyl group by digestion with an alcoholic solution of potash, giving β-hydroxypropylphthalimide, X:

$$C_6H_4(CO)_2NCH_2CHBrCH_3 + KOH = KBr + C_6H_4(CO)_2NCH_2.CHOH.CH_3 \text{ (X.)}$$

He apparently obtained no evidence of the formation of an allyl or a propenyl derivative by removal of hydrobromic acid.

These observations suggested to the writer that β-brompropylphthalimide would react normally with the sodium salt of an acid methylene compound, —CO—CH_2—CO—. For example, theoretically it would be expected to combine with the sodium salt of diethyl malonate, giving the unknown diethyl β-methyl-γ-phthalimidoethylmalonate, XI:

$$C_6H_4(CO)_2NCH_2.CHBr.CH_3 + NaCH(COOC_2H_5)_2 = C_6H_4(CO)_2N.CH_2CH(CH_3)CH(COOC_2H_5)_2 \text{ (XI.)}$$

The isomeric diethyl phthalimidopropylmalonate, XII, has been synthesized by Gabriel[2] by the action of the isomeric γ-brompropylphthalimide on diethyl sodiummalonate:

[1] Ber. d. chem. Ges., **40**, 4400 (1907).
[2] *Ibid.*, **23**, 1768 (1890).

$$C_6H_4(CO)NCH_2CH_2CH_2Br + NaCH(COOC_2H_5)_2 = C_6H_4(CO)_2NCH_2CH_2CH_2CH(COOC_2H_5)_2.$$
XII.

We now find that β-brompropylphthalimide does not react with diethyl sodiummalonate like its isomer, giving the ester, XI, but loses a molecule of hydrobromic acid under these conditions, giving a good yield of the hitherto unknown *propenylphthalimide*, XIII, with regeneration of diethyl malonate:

$$C_6H_4(CO)_2NCH_2CHBrCH_3 + NaCH(COOC_2H_5)_2 = NaBr + CH_2(COOC_2H_5)_2 + C_6H_4(CO)_2N.CH:CHCH_3.$$
XIII.

We furthermore have obtained evidence which indicates that there are two isomeric modifications of propenylphthalimide. Two compounds having this empirical formula were isolated and had the same melting point, but they differed in color, crystalline form and solubility. Owing to the fact, however, that one of the isomers was not obtained in sufficient quantity for a careful examination it was impossible to establish definitely the nature of this isomerism. It seems very probable, nevertheless, that we are dealing here with a case of isomerism similar in character to that observed by Wislicenus[1] in the case of the stereoisomeric butylenes, XVI and XVII, and by Hoering and Baum[2] in the case of the isosafroles, XVIII and XIX.

$C_6H_4(CO)_2N.C.H$ ‖ $CH_3.C.H$ — XIV.

$C_6H_4(CO)_2N.C.H$ ‖ $H.C.CH_3$ — XV.

$CH_3.C.H$ ‖ $CH_3.C.H$ — XVI.

$CH_3.C.H$ ‖ $H.C.CH_3$ — XVII.

$CH_3O_2C_6H_3.C.H$ ‖ $CH_3.C.H$ — XVIII.

$CH_3O_2C_6H_3.C.H$ ‖ $H.C.CH_3$ — XIX.

[1] Ann. Chem. (Liebig), **313**, 207 (1900).
[2] Ber. d. chem. Ges., **42**, 3076 (1909).

Several attempts were made to prepare propenylphthalimide by the action of other reagents than diethyl sodiummalonate on β-brompropylphthalimide. The halide, however, showed a remarkable inertness in many cases where a reaction would be expected to take place. No evidence of the formation of allyl- or propenylphthalimide was obtained when the bromide was warmed in alcohol with metallic zinc or silver benzoate or when digested with boiling pyridine. Sodium phenolate, on the other hand, reacted immediately with the bromide, on warming in alcoholic solution, giving the propenyl compound.

Propenylphthalimide is characterized by its yellow color, while the isomeric allyl compound is colorless. It is less soluble in alcohol than allylphthalimide and melts at 151°. It does not add hydrobromic acid to give the original β-brompropylphthalimide and does not rearrange to the isomeric allyl derivative when heated above its melting point. Allylphthalimide is not transformed into propenylphthalimide by treatment with alcoholic potash. This observation is of interest because it shows that allylphthalimide is not an intermediate product of the reaction when β-brompropylphthalimide undergoes conversion to the propenyl compound by the action of diethyl sodiummalonate. On the other hand it undergoes saponification under these conditions, giving smoothly the corresponding allylphthalamic acid, XX, melting at 112°. Allyl- and propenylphthalimides are converted into allylphthalamic acid, XX, and propenylphthalamic acid, XXI, (melting at 151°), respectively, when warmed with sodium ethylate:

$$\underset{\text{XX.}}{HOOCC_6H_4CONHCH_2CH:CH_2}, \quad \underset{\text{XXI.}}{HOOCC_6H_4CONHCH:CHCH_3}.$$

The regularity with which the removal of halogen acids takes place in certain halogen compounds, giving ethylene derivatives, led in early years to the formulation of rules governing the manner of removal which might be expected to take place. One of these is as follows: "*When the halogen atom is between two hydrogenated carbon atoms, the hydrogen is removed from that carbon having the least number of hydrogen*

atoms."[1] It was of interest in connection with our work to make a classification of certain types of halides in order to determine the general application of this rule. A careful review of the literature now reveals the fact that the majority of halides of the general formula under examination,

$$X.CH_2.CH\ hal.CH_3,$$

lose the halogen acid in conformity with the above rule, as we have observed in the case of β-brompropylphthalimide. There are, however, several exceptions which are of interest.

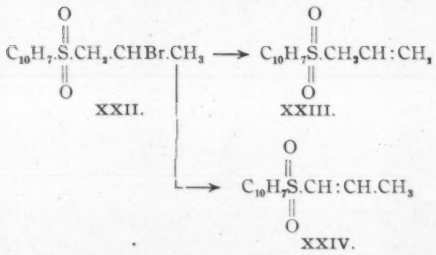
It is therefore interesting to note in this connection that, of 27 different halides of the above type which we have reviewed, 17 have undergone transformations by the action of alkali and other reagents, giving propenyl compounds. The most striking feature of this list of 17 halides (Table I) is the variety of organic radicals which have been substituted for X. An examination of the tables will show conclusively that an unsaturated condition, or the positive and negative character of the groups X, are not the deciding factors in governing the position the double bond will take.

The radicals substituted for X (Table II) which have favored the formation of allyl compounds among this series of 27 halides are represented only by β-naphthylsulfone, $C_{10}H_7SO_2$, hippuryl, $C_6H_5CONHCH_2CO$, and a series of aminoalkyl groups,[2] in which the amino radical occupies positions 4 or 5 with respect to the halogen atom. It is especially noteworthy that α-naphthylsulfone-β-brompropane,[3] XXII, should give an allyl derivative, XXIII, since it represents a type of compounds which theoretically would be expected to give propenyl derivatives, XXIV.

[1] Beilstein's Handbuch, I, 95; and Alexeyeff and Mathews: General Principles of Organic Synthesis, pp. 108.

[2] Merling: Ann. Chem. (Liebig), **264**, 310 (1891). Jacobi and Merling: *Ibid.*, **278**, 1 (1893).

[3] Troeger and Artmann: J. prakt. Chem., **53**, 492 (1896).



That β-brompropylhippurylamide,[1] XXV, should react with sodium ethylate and diethyl sodiummalonate, giving an allyl derivative, XXVI, while β-brompropylphthalimide, under the same conditions, gives a propenyl compound, is truly remarkable. Apparently it is the only acylamide of this type which has been observed to break down in this manner, giving an ethylene compound. Compounds of this type usually decompose, in the presence of alkali, in a characteristic way, giving oxazolines:[2]

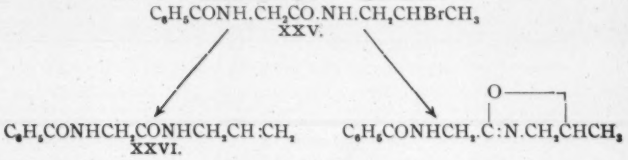


Table I.

Organic radicals which favor the formation of propenyl compounds: $X.CH_2.CHhal.CH_3 \longrightarrow X.CH:CH.CH_3$.

X = CH_3,[3] C_2H_5,[4] C_3H_7,[5] C_4H_9,[6] $CH_2:CH.CH_2$,[7] CH_3CO,[8]

[1] Diels and Beccard: Ber. d. chem. Ges., **39,** 4126 (1906).

[2] Gabriel: *Ibid.*, **22,** 2984. Gabriel and Heymann: *Ibid.*, **23,** 2493. Gabriel and Lauer: *Ibid.*, **23,** 91. Prager: *Ibid.*, **22,** 2991. Hirsch: *Ibid.*, **23,** 964. Elfeldt: *Ibid.*, **24,** 3218.

[3] Luynes: Ann. Chem. (Liebig), **128,** 331.

[4] Wurtz: *Ibid.*, **123,** 203; **127,** 55; **148,** 131. Wagner and Saytzew: *Ibid.*, **175,** 373; **179,** 302.

[5] Erlenmeyer and Wanklyn: *Ibid.*, **135,** 134. Hecht and Munier: Ber. d. chem. Ges., **11,** 1154.

[6] Schorlemmer: Ann. Chem. (Liebig), **166,** 177.

[7] Grinner: Beilstein's Handbuch, I, 133.

[8] Blaise: Bull. soc. chim., [3] **33,** 45.

NH_2,[1] $C_2H_5O(NH)C$,[2] NH_2CO,[2] $C_6H_5CH_2NH(?)$,[3] $COOH$,[4] C_6H_5,[5] $C_6H_4.CH_3$,[5] Br,[6] $BrCH_2.CH_2$,[6] $CH_3CHBr.CH_2$,[7] CH_3CHCH_3.[7]

Table II.

Organic radicals which favor the formation of allyl compounds: $X.CH_2.CHhal.CH_3 \longrightarrow X.CH_2.CH:CH_2$.

$X = NH_2CH_2$,[8] $NH_2(CH_3)CHCH_2$, $NH_2(CH_3)CHCH(CH_3)$, $NH_2(CH_3)CHCH(CH_2CH:CH_2)$, $N(CH_3)_2CH_2CH_2$, $N(CH_3)_2(CH_2)_2CH_2$, $N(CH_3)_2(CH_3)CHCH_2$, $N(CH_3)_2CH_2CH(CH_3)$,[9] $C_6H_5CONHCH_2CONH$,[10] $C_{10}H_7SO_2$.[11]

EXPERIMENTAL PART.

Allylphthalimide, $C_6H_4(CO)_2N.CH_2CH:CH_2$.—This compound was prepared according to Kay's[12] method by heating allyl isothiocyanate with phthalic anhydride:

$$C_6H_4(CO)_2O + CH_2:CHCH_2NCS = C_6H_4(CO)_2NCH_2.CH:CH_2 + COS.$$

Thirty grams of freshly distilled allyl isothiocyanate were mixed with 46.8 grams (1 mol.) of finely powdered phthalic anhydride and heated in an oil bath at 135°–140°. The anhydride soon went into solution, giving a yellow liquid. After heating for about 70 hours, when the evolution of carbon oxysulphide had practically ceased, the liquid was then cooled and washed several times with hot water, to remove phthalic acid. The allylphthalimide then solidified and was purified by distillation under diminished pressure and recrystallization from carbon bisulphide. It crystallized in large colorless prisms which melted at 71° to an oil. Allylphthalimide is

[1] Hirsch: Ber. d. chem. Ges., **23,** 968.
[2] Pinner: *Ibid.*, **17,** 2008.
[3] Uedinck: *Ibid.*, **32,** 972.
[4] Balbiano: *Ibid.*, **11,** 348. Pinner: *Ibid.*, **12,** 2058.
[5] Errara: Gazz. chim. ital., **14,** 318: **14,** 283.
[6] Solinina: J. russ. physik. chem. Ges., **30,** 862. Centralb., **1899,** I, 248.
[7] Schramm: Ber. d. chem. Ges., **30,** 637.
[8] Leuchmann: Ber. d. chem. Ges., **29,** 1431.
[9] Jacobi and Merling: *Loc. cit.*
[10] Diels and Baccard: *Loc. cit.*
[11] Troeger and Artmann: *Loc. cit.*
[12] Ber. d. chem. Ges., **26,** 2850 (1893).

very soluble in ether, carbon bisulphide, benzene, petroleum ether and alcohol, and insoluble in water. It can be crystallized from alcohol. The total yields and relative proportions of allylphthalimide obtained in four experiments by the above method are given in the following table:

	Phthalic anhydride. Grams.	Allyl isothiocyanate. Grams.	Yield of allylphthalimide. Grams.	Yield. Per cent.
1	56.0	33.7	41.0	58.5
2	36.5	22.5	30.5	66.1
3	40.5	25.0	34.5	67.4
4	48.6	30.0	48.0	78.1

β-Brompropylphthalimide,[1] $C_6H_4(CO)_2N.CH_2.CHBr.CH_3$.—When allylphthalimide is suspended in a strong hydrobromic acid solution, addition of hydrobromic acid to the double bond takes place immediately. We found, however, that our yields of the above bromide were greatly improved by using an acid which had been saturated with hydrobromic acid gas at —5° to 0°. The best yields were obtained under the following conditions: Thirty grams of pulverized allylphthalimide were suspended, in a strong, glass-stoppered bottle, in 150 cc. of hydrobromic acid saturated with hydrobromic acid gas at —5°. Practically all of the phthalimide dissolved in a few minutes, giving a clear solution. After standing at room temperature for two or three days, with occasional shaking, a dense mass of crystals separated, which were filtered on asbestos by suction, washed with cold water and allowed to dry in the air. The crude product usually melted sharply at 105° to a clear oil. It melted, after purification by recrystallization from alcohol, at 110°.

β-Brompropylphthalimide crystallizes from 95 per cent. ethyl alcohol in colorless, fibrous, glistening needles. It is easily soluble in ethyl and methyl alcohols, carbon bisulphide, ether, chloroform and benzene and slightly soluble in petroleum ether and boiling water. The yields and relative proportions of β-brompropylphthalimide obtained in three preparations are given in the following table:

[1] Seitz: *Loc. cit.*

	HBr. cc.	Allylphthalimide. Grams.	Yield of bromopropylphthalimide. Grams.	Yield. Per cent.
1	200	47.0	55.0	81.6
2	150	30.0	30.0	70.0
3	124	31.0	35.0	78.8

Action of Diethyl Sodiummalonate on β-Brompropylphthalimide.

Formation of Propenylphthalimide, $C_6H_4(CO)_2N.CH:CH.CH_3$. —Thirty-one and three-tenths grams of diethyl malonate were added to a cold solution of sodium ethylate, prepared by dissolving 4.5 grams of sodium in 250 cc. of absolute alcohol. Fifty-two and three-tenths grams of β-brompropylphthalimide were then dissolved in the solution and the mixture digested on the steam bath for two hours, when the solution reacted neutral to litmus and turmeric. After filtering off the undissolved sodium bromide, the solution was concentrated under diminished pressure and the residue obtained then extracted with a small volume of ether. A crystalline substance, insoluble in ether, was obtained here, which was separated by filtration, washed with cold water and purified by crystallization from alcohol (see below for the examination of the ether filtrate). The compound separated on cooling in characteristic, light-yellow blocks, which melted at 151° to an oil. The analytical determinations gave the following results:

I. Nitrogen determinations by Kjeldahl method.

II. 0.1280 gram substance gave 0.3327 gram CO_2 and 0.0603 gram H_2O.

	Calculated for $C_{11}H_9O_2N$.	Found. I.	II.
C	70.58	70.89	....
H	4.81	5.27	....
N	7.48	7.38	7.16

Molecular weight determination in benzene solution:

0.6670 gram of substance dissolved in 14.11 grams benzene caused a depression of 1°.283 in the freezing point of the solvent.

	Calculated for $C_{11}H_9O_2N$.	Found.
Mol. weight	187	180.6

A solution of propenylphthalimide decolorized bromine water at once. It is readily soluble in benzene, chloroform and carbon bisulphide; moderately soluble in alcohol and insoluble in petroleum ether and water. The yellow color of the crystals is apparently characteristic and not due to impurities. The yield of purified material was 8 grams.

Examination of the Above Ether Filtrate.—When this was allowed to evaporate in air we obtained a colorless oil, from which about 5 grams of the propenyl derivative, mixed with a little β-propylphthalimide, deposited on standing. The oil was dissolved in petroleum ether, dried over sodium sulphate and then purified by distillation. We obtained 19 grams of unaltered diethyl malonate boiling at 194°-202°, which represented about 60 per cent. of the original ester used. The dark-colored oily residue which remained in the distilling bulb had the properties of an acid and dissolved in cold alkali with the exception of a small amount of crystalline material. This was separated, dissolved in hot alcohol, and some benzene added to the solution, when about 0.5–0.7 gram of large, colorless, glistening, micalike plates separated. This substance did not contain bromine and melted at 150°–151°, to an oil. A mixture of this compound and the propenyl compound melted at the same temperature. It was very soluble in alcohol and moderately soluble in benzene. Nitrogen and molecular weight determinations proved that it was isomeric with propenylphthalimide. Owing to the fact, however, that the yield of this interesting substance was so small, it was impossible to make a thorough study of its properties. Whether it is a stereoisomeric modification or a physical isomer we are unable to say at the present time. Nitrogen determinations by Kjeldahl method:

	Calculated for $C_{11}H_9O_2N$.	Found. I.	Found. II.
N	7.48	7.18	7.3

Molecular weight determination in benzene solution:

0.3254 gram of substance dissolved in 12.27 grams of benzene caused a depression of 0°.719 in the freezing point of the solvent.

	Calculated for $C_{11}H_9O_2N$.	Found.
Mol. weight	187	180.7

Action of Sodium Phenolate on β-Brompropylphthalimide.

Formation of Propenylphthalimide.—Two grams of the bromide and 0.7 gram of phenol, in the form of sodium phenolate, were dissolved in absolute alcohol and digested on the steam bath for 6–7 hours. The solution was then cooled and the undissolved sodium bromide filtered off. On concentrating the alcohol filtrate a viscous liquid was obtained which we triturated with water to remove any sodium bromide held in solution. On standing, this oil partially solidified and deposited a yellow crystalline substance which crystallized from 95 per cent. alcohol. More of the substance continually separated on standing. The compound separated from alcohol, on cooling, in stout, yellow blocks which melted at 150°–151° to a clear oil, without effervescence. It was identified as propenylphthalimide. A mixture of this substance and a sample of propenylphthalimide described in the preceding experiment melted at exactly the same temperature.

Nitrogen determination (Kjeldahl):

	Calculated for $C_9H_{11}O_3N$.	Found.
N	7.48	7.4

Action of Sodium Ethylate on Propenylphthalimide.

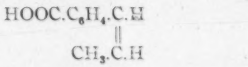
Formation of Propenylphthalamic Acid, $HOOC.C_6H_4.CONHCH:CH.CH_3$.—Two grams of propenylphthalimide were added to a solution of sodium ethylate prepared by dissolving 0.72 gram of sodium (1 molecule) in 25 cc. of absolute alcohol. After 2 hours' digestion the alcohol was then evaporated when a syrupy residue was obtained. This was dissolved in cold water and the solution acidified with hydrochloric acid, when a red oil separated which dissolved immediately in ether. When the ether was allowed to evaporate 1.6 grams of the phthalamic acid separated as a crystalline powder. It is ex-

tremely soluble in water and alcohol and difficultly soluble in ether; insoluble in petroleum ether, benzene and chloroform. When it is dissolved in absolute alcohol and the solution allowed to evaporate at ordinary temperature the acid separates as a thick, viscous syrup which finally crystallizes after long standing. It melts at 152° to a clear oil.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3N$.	Found. I.	II.
N	6.83	6.73	6.7

Propenylphthalamic acid is precipitated from an alkaline solution by addition of hydrochloric acid as a viscous substance, which assumes, slowly, a crystalline condition only after long standing. This is the most characteristic property of this acid. The fact that the allylphthalamic acid shows no tendency to undergo such changes under the same conditions suggests that we have here two stereoisomeric modifications of propenylphthalamic acid, one form a syrup at ordinary temperature and the other a solid melting at 152°. Whether the solid melting at 152° represents the *cis* or *trans* modification we have no evidence.



This syrupy, labile propenylphthalamic acid is undoubtedly one of the products of the reaction when diethyl sodiummalonate acts on β-brompropylphthalimide. A viscous oil having acid properties is always obtained in this reaction and the quantity formed varies according to the conditions employed. Its formation explains the fact that unaltered β-brompropylphthalimide is always present even after the tests with turmeric and litmus indicate a neutral reaction.

Action of Sodium Ethylate on β-Brompropylphthalimide.—Three grams of β-brompropylphthalimide and 0.26 gram of sodium were dissolved in 15 cc. of absolute alcohol and the solution digested until neutral to turmeric (1.5 hours). On cooling, a mixture of sodium bromide and unaltered β-brom-

propylphthalimide separated. They were separated by filtration and washed with water to remove sodium bromide, when we recovered 1.0 gram of the β-brompropylphthalimide melting at 110°. The alcoholic filtrate was concentrated to a syrup, which was dissolved in cold water and filtered. The addition of hydrochloric acid precipitated a heavy, viscous oil, which possessed all the properties of labile propenylphthalamic acid. It did not contain bromine. We obtained no evidence of the formation of any allyl- or propenylphthalimide.

β-Brompropylphthalimide was recovered unaltered after digestion in benzene with zinc dust for 6 hours, and also after digestion in alcohol for 14 hours with silver benzoate. One gram was dissolved in 4 cc. of pyridine and the solution boiled for 5 hours. Water was then added to the cooled solution when the unaltered bromide separated and melted at 108°–110° without further purification.

Action of Sodium Ethylate on Allylphthalimide.

Formation of Allylphthalamic Acid, $HOOC.C_6H_4.CO.NH.CH_2.CH:CH_2$.—Five grams of allylphthalimide and 1.2 grams of sodium were dissolved in 50 cc. of absolute alcohol and the solution heated on a boiling water bath for 2 hours. On cooling, the sodium salt of allylphthalamic acid separated. The excess of alcohol was removed by evaporation, the salt dissolved in water and the solution acidified with hydrochloric acid. The allylphthalamic acid separated at once in crystalline form and melted at 112° to oil. This melting point was not changed by further attempts at purification. The acid is insoluble in cold ether, but extremely soluble in warm water, alcohol and benzene. It crystallizes best from a mixture of alcohol and ether.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3N$.	Found.
N	6.83	6.68

This same acid is also obtained in the form of its potassium salt by gentle warming of allylphthalimide with the calculated

amount of potassium hydroxide in alcohol. If digested with alkali for a prolonged period on the water bath, it undergoes complete decomposition, giving allylamine and *o*-phthalic acid melting at 199°. We obtained no evidence of any formation of propenylphthalimide or propenylphthalamic acid.

NEW HAVEN, CONN.,
Dec. 24, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXIX.—RESEARCHES ON PYRIMIDINES: ON THE CONDENSATION OF THIOUREA WITH ESTERS OF ALLYLMALONIC ACID AND SOME ALKYL-SUBSTITUTED ALLYLMALONIC ACIDS.

BY TREAT B. JOHNSON AND ARTHUR J. HILL.

[FIFTIETH PAPER.]

In this paper we describe a number of new condensation products which we have obtained by condensing thiourea with diethyl allylmalonate,[1] I, diethyl allylbenzylmalonate, II, and diethyl diallylmalonate,[2] III.

$$CH_2{:}CHCH_2CH(COOC_2H_5)_2$$
I.

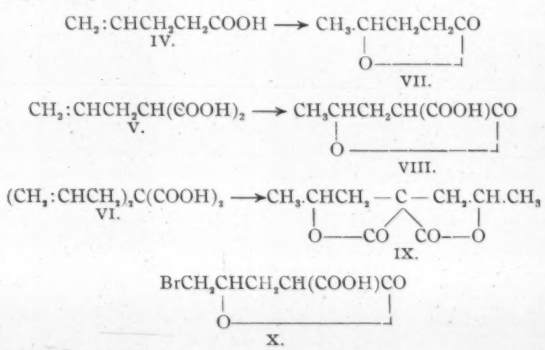
$$CH_2{:}CHCH_2(C_6H_5CH_2)C(COOC_2H_5)_2$$
II.

$$(CH_2{:}CHCH_2)_2C(COOC_2H_5)_2$$
III.

It is a well-known fact that unsaturated acids—olefincarboxylic acids—which contain a double bond between the γ,δ positions, easily undergo isomerization to γ-lactones. This change can be effected in different ways, as by distillation of the unsaturated acid, by addition of a halogen acid and its subsequent removal with closing of the ring, or by warming of the acid with dilute sulphuric acid. The simplest unsaturated monobasic and dibasic acids of this type, viz., allylacetic, IV, allylmalonic, V, and diallymalonic, VI, for example, are all transformed smoothly, under proper conditions,

[1] Conrad and Bischoff: Ann. Chem. (Liebig), **204**, 168.
[2] Conrad and Bischoff: *Loc. cit.*

into γ-methylbutyrolactone,[1] VII, γ-methylbutyrolactone-α-carboxylic acid.,[2] VIII, and γ,γ-dimethyldibutyrolactone,[3] IX, respectively.



Fittig and Hjelt,[4] who investigated very thoroughly the action of hydrobromic acid and bromine on allyl fatty acids, were unable to obtain, in a pure state, γ-brompropylmalonic, XI, or γ,δ-dibrompropylmalonic, XII, acids by addition

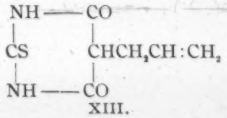
$$\underset{\text{XI.}}{CH_3CHBrCH_2CH(COOH)_2}, \qquad \underset{\text{XII.}}{BrCH_2.CHBr.CH_2CH(COOH)_2}$$

of hydrobromic acid and bromine, respectively, to allylmalonic acid. They both underwent decomposition, even at ordinary temperature, giving the corresponding γ-methylbutyrolactone-α-carboxylic acid, VIII, and γ-brommethylbutyrolactone-α-carboxylic acid, X. Furthermore, they observed also that the formation of γ-lactones was not prevented by using the esters instead of the acids. The same lactone, for example, was obtained by the action of bromine on diethyl diallylmalonate as was obtained by the addition of bromine to the corresponding acid.

[1] Messerschmidt: Ann. Chem. (Liebig), **208,** 97.
[2] Hjelt: *Ibid.*, **216,** 53.
[3] Hjelt: *Loc. cit.*
[4] Ann. Chem. (Liebig), **216,** 52. Hjelt: Ber. d. chem. Ges., **15,** 627.

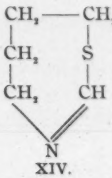
Owing to this instability of the γ- and γ,δ-halogen substituted propylmalonic acids, they are of limited value for synthetical purposes. A derivative, therefore, of allylmalonic acid, in which the carboxyl groups are linked in a manner so as to prevent lactone formations after addition of halogen acids and halogens to the ethylene linking, would be of especial interest. With the object in view of preparing a compound of this type, we therefore examined the behavior of diethyl allylmalonate towards thiourea. Theoretically they would be expected to react normally, giving the unknown allylthiobarbituric acid, XIII:

$CH_2{:}CHCH_2CH(COOC_2H_5)_2 + CS(NH_2)_2 =$

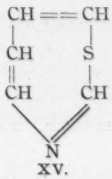


XIII.

We now find that diethyl allylmalonate condenses in a unique manner with thiourea, giving a stable, cyclic derivative—μ-amino-α-keto-β-carbethoxy-δ-methyltetrahydrohexathiazole, XVIII. This is a representative of a new class of cyclic compounds, tetrahydrohexathiazoles, XIV, of which the mother substance would be the *hexathiazole*[1] XV. Derivatives of analogous, six-membered rings containing sulphur and oxygen, viz., *penthiazolines*, XVI, and *pentoxazolines*, XVII, have been synthesized by Gabriel and his coworkers.[2]



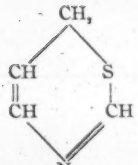
XIV.



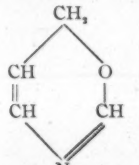
XV.

[1] Nomenclature: Traumann: Ann. Chem. (Liebig), **249**, 34. Krekeler: Ber. d. chem. Ges., **19**, 3266.

[2] Gabriel and Lauer: Ber. d. chem. Ges., **23**, 95. Gabriel and Elfeldt: *Ibid.*, **24**, 3213. Elfeldt: *Ibid.*, **24**, 3218.

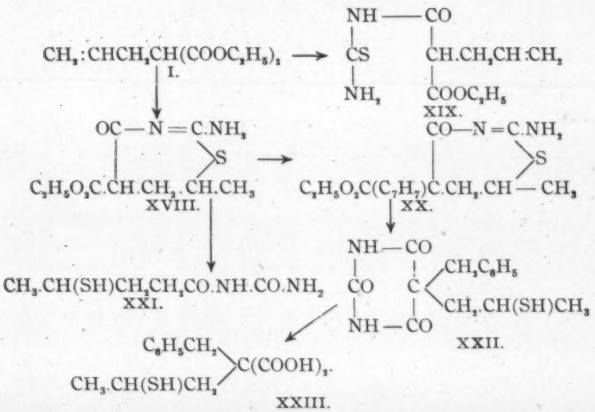


XVI.

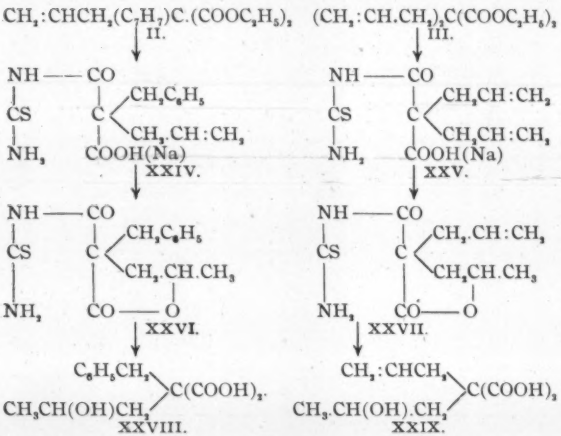


XVII.

That diethyl allylmalonate condensed, giving a *tetrahydrohexathiazole* derivative, XVIII, and not the isomeric thiourea compound, XIX, was established by the following facts: The hexathiazole, XVIII, was not desulphurized by the action of mercury oxide or lead acetate, indicating a linking of the sulphur atom between two carbon atoms. It behaved as a pseudo-thiourea and underwent hydrolysis, in acid solution, giving γ-mercapto-*n*-valerylurea, XXI. The compound reacted with benzyl chloride, in presence of sodium ethylate, giving a benzyl derivative, substituted on the carbon, XX. This alkyl derivative was converted quantitatively into 5,5-benzyl-β-mercaptopropylbarbituric acid, XXII, by hydrolysis with concentrated hydrochloric acid. Saponification of this pyrimidine with strong potash then gave smoothly the hitherto unknown β-mercaptopropylbenzylmalonic acid, XXIII. These reactions prove that thiourea reacts in its pseudo form with diethyl allylmalonate, and that the mercapto group –SH adds at the double bond of the allyl group, giving the cyclic derivative, XVIII. These various transformations are represented by the following formulas:



In order to determine whether alkyl derivatives of diethyl allylmalonate would condense with thiourea, in a similar manner as allylmalonic ester, giving the corresponding tetrahydrohexathiazoles, we also examined the behavior of diethyl allylbenzylmalonate, II, and diethyl diallylmalonate, III, towards this reagent. We now find that these two esters react with thiourea in an entirely different manner than diethyl allylmalonate. They condense practically quantitatively, in the presence of sodium ethylate, giving apparently the sodium salts of the corresponding acylthioureas, XXIV and XXV. When these salts were dissolved in water and the solutions acidified with hydrochloric or sulphuric acids, the acids immediately underwent isomerization to the corresponding γ-lactones, XXVI and XXVII. Their low melting points indicated a lactone structure, and they were desulphurized by the action of mercury oxide. Their constitution was established by the facts that they underwent a normal lactone hydrolysis, with potassium hydroxide, giving the corresponding β-hydroxypropylbenzylmalonic, XXVIII, and β-hydroxypropylallylmalonic, XXIX, acids, respectively, with formation of ammonia and hydrogen sulphide. These various changes are represented in the following manner:

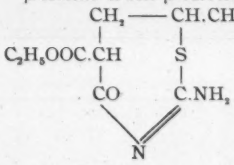


The observation that the two acids XXIV and XXV undergo isomerization, giving apparently γ-lactones, instead of condensing in a normal manner to give barbituric acid derivatives, is especially interesting. It is also a remarkable fact that thiourea reacts with diethyl allylmalonate with addition of –SH at the double bond of the allyl group, while the corresponding diallyl compound shows no tendency, under the same conditions, to give a tetrahydrohexathiazole, but condenses to a γ-lactone.

The study of the action of esters of unsaturated acids on thioureas, ureas, pseudothioureas and guanidines is being continued in this laboratory.

EXPERIMENTAL PART.

μ-Amino-α-keto-β-carbethoxy-δ-methyltetrahydrohexathiazole.—



.—Three and six-tenths grams of

sodium were dissolved in 40 cc. of absolute alcohol and 4.5 grams of thiourea added to the solution. Fifteen grams of diethyl allylmalonate (1 molecule) were then added and the solution heated in a boiling water bath. There was an immediate reaction and within a few minutes a magma of a colorless sodium salt was obtained. The mixture was then heated for 5 to 7 hours in order to complete the reaction and the excess of alcohol finally expelled by evaporation at 100°. The salt was then dissolved in the least possible quantity of cold water and an excess of dilute sulphuric acid added, and the solution cooled to 0°. The hexathiazole separated as a pink, crystalline precipitate. The compound was extremely soluble in alcohol and was purified by crystallization from hot water in which it is quite soluble. The aqueous solution must not, however, be heated to boiling as the compound slowly undergoes hydrolysis under these conditions, giving an oily, ill-smelling compound. On cooling it separates in pink-colored prisms, which melt at 88°–89° to a clear oil. The yield was 12.7 grams. The hexathiazole is not desulphurized by warming in aqueous and alcoholic solutions with mercury oxide, or with lead acetate in an alkaline solution. It dissolves in dilute sodium hydroxide solution, giving a characteristic purple-red solution which changes, on heating, to the color of a dilute Congo-red solution. It is not decomposed by boiling in alkaline solution and is precipitated unaltered on making the solution acid. The stability of the compound towards alkali was remarkable.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_9H_{14}O_2N_2S$.	Found. I.	II.	III.
N	12.17	12.24	12.24	12.2

Hydrolysis with Hydrochloric Acid.

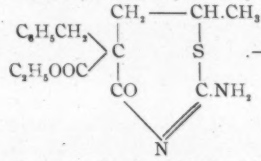
Formation of γ-Mercapto-n-valerylurea, $CH_3.CH(SH).CH_2CH_2.CO.NH.CO.NH_2$.—This compound was obtained by dissolving 1.8 grams of the above hexathiazole in 50 cc. of cold concentrated hydrochloric acid and then evaporating the solution to dryness on the steam bath. It is insol-

uble in cold water but soluble in warm absolute alcohol. It was purified for analysis by recrystallization from glacial acetic acid and melted at 186° with decomposition.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_8H_{13}O_3N_3S$.	Found. I.	Found. II.
N	16.00	16.2	16.2

μ-Amino-α-keto-β-carbethoxy-δ-methyl-β-benzyltetrahydrohexathiazole,

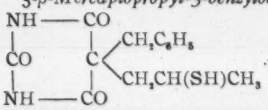


.—Sixty-two hundredths gram of sodium was dissolved in absolute alcohol and 6.2 grams of α-keto-β-carbethoxy-δ-methyl -μ- aminotetrahydrohexathiazole added to the solution, when the corresponding sodium salt separated at once. A molecular proportion of benzyl chloride (3.4 grams) was then added and the mixture heated until neutral to turmeric. The reaction was complete within a few minutes and after evaporating the excess of alcohol the benzylhexathiazole was purified by crystallization from 50 per cent. alcohol. It separated, on cooling, in colorless prisms melting at 221° to an oil without effervescence. The compound is soluble in boiling alcohol but insoluble in water. The yield of purified material was 4.0 grams.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{15}H_{20}O_3N_2S$.	Found. I.	Found. II.
N	8.75	8.76	8.73

5-β-Mercaptopropyl-5-benzylbarbituric Acid,



.—A quantitative yield of this pyrimidine was obtained by dissolving 4 grams of the above benzylhexathiazole in 50 cc. of cold, concentrated

hydrochloric acid and then evaporating the solution to dryness on the steam bath. It is insoluble in cold water and alcohol, but crystallizes from glacial acetic acid in colorless prisms melting at 236° to an oil. The pyrimidine is not decomposed by short digestion with 50 per cent. potash solution, and separated unaltered on the addition of hydrochloric acid. It gave a strong test for sulphur.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{14}H_{16}O_2N_2S$.	Found. I.	II.
N	9.59	9.5	9.7

β-Mercaptopropylbenzylmalonic Acid, $C_6H_5CH_2$ $CH_2.CH(SH)CH_2$ $>C(COOH)_2$.—This acid was obtained in the form of its monopotassium salt as follows: 2 grams of the above pyrimidine were dissolved in 6 cc. of a 50 per cent. potassium hydroxide solution and heated in a sealed tube at 130° for two hours. A clear solution was obtained having a strong odor of ammonia. Hydrochloric acid was then added in excess, when a characteristic, crystalline monopotassium salt of the malonic acid separated from the acid solution. There was no evidence of any evolution of hydrogen sulphide. The substance left a heavy inorganic residue when burned on a platinum foil and gave a positive test for sulphur.

Sulphur determination (Carius):

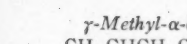
I. 0.1157 gram of substance gave 0.0891 gram of $BaSO_4$.

	Calculated for $C_{12}H_{12}O_4SK$.	Found.
S	10.45	10.58

Diethyl Allylbenzylmalonate, $C_6H_5CH_2$ $CH_2:CH.CH_2$ $>C(COOC_2H_5)_2$.—This ester was prepared by the action of allyl iodide on the sodium salt of diethyl benzylmalonate[1] in alcoholic solution, and also by the action of benzyl chloride on diethyl sodium-allylmalonate[1]. It is a colorless viscous oil which boils at 228°–230° under 60–65 mm. pressure.

[1] Conrad and Bishoff: *Loc. cit.*

γ-Methyl-α-benzylbutyrolactone-α-carboxylic Acid,



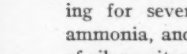
.—This was obtained as a syrup by saponification of diethyl allylbenzylmalonate: 1.7 grams of the ester were dissolved in 50 per cent. alcohol containing three molecular proportions of potassium hydroxide, and the solution boiled for one hour. After acidifying strongly with hydrochloric acid the solution was extracted repeatedly with ether and the latter then evaporated. A thick syrup was obtained which did not crystallize after standing for several hours. This was dissolved in cold, dilute ammonia, and the silver salt precipitated by adding an excess of silver nitrate solution. It separated as a colorless, granular precipitate, which was dried for analysis in a desiccator over concentrated sulphuric acid.

Silver determination:

I. 0.1894 gram substance gave 0.0722 gram Ag.

	Calculated for $C_{12}H_{13}O_4Ag$.	Found.
N	31.7	32.8

γ-Methyl-α-benzylbutyrolactone-α-carbonylthiourea,



.—One gram of sodium (2 molecules) was dissolved in 20 cc. of absolute alcohol and a molecular proportion of thiourea (1.6 grams) dissolved in the solution; 6.1 grams of diethyl allylbenzylmalonate were then added and the solution heated at 100° for five hours. We obtained a turbid solution which was heated in an open vessel to expel the excess of alcohol, and the sodium salt dissolved in water. On acidifying with hydrochloric acid a heavy, yellow, semisolid product separated which assumed a crystalline form on trituration with a little benzene. The lactonethiourea is soluble in warm alcohol and moderately soluble in benzene. It crystallizes from the latter in light yellow crystals which melt at 145°–146° to a clear oil without effervescence. It dissolves in cold concentrated hydrochloric acid and the

solution can be evaporated to dryness without decomposition of the lactone.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_{14}H_{16}O_4N_2S$.	Found. I.	Found. II.
N	9.56	9.55	9.62

β-Hydroxypropylbenzylmalonic Acid,

$C_6H_5CH_2$
$CH_2.CH(OH).CH_2$ >C(COOH)$_2$.—Two grams of the preceding γ-lactone were dissolved in 6 cc. of a 50 per cent. potassium hydroxide solution and heated for two hours at 130°–150°. Ammonia was given off and when the solution was acidified with hydrochloric acid hydrogen sulphide gas was evolved, and a viscous substance separated. This was dissolved in ether, dried over anhydrous sodium sulphate and the ether evaporated, when we obtained the malonic acid as an oil which did not crystallize. This was dissolved in cold, dilute ammonia and the acid precipitated in the form of its disilver salt by addition of an excess of silver nitrate solution. The salt separated as a flocculent precipitate which was washed with a little water and alcohol, and then dried for analysis in a desiccator over sulphuric acid.

Silver determination.

I. 0.1105 gram substance gave 0.0508 gram Ag.

	Calculated for $C_{12}H_{14}O_5Ag_2$.	Found.
Ag	46.3	45.9

γ-Methyl-α-allylbutyrolactone-α-carbonylthiourea,

$CH_3.CH.CH_2C(CH_2CH:CH_2).CONHCSNH_2$
$O——CO$.—This compound was prepared in a similar manner as the corresponding α-benzyl compound by condensing 10.8 grams of diethyl diallylmalonate with 3.4 grams of thiourea in presence of 2.1 grams of sodium dissolved in 50 cc. of alcohol. After removal of the excess of alcohol, the sodium salt was then dissolved in cold water and the thiourea liberated by addition of dilute

sulphuric acid. It separated as a semisolid substance, which finally crystallized. It is desulphurized by digestion in aqueous solution with mercury oxide. The thiourea was purified by crystallization from boiling acetic acid or water, from which it separated in cream-colored plates melting at 134°–135° to an oil. When dissolved in concentrated hydrochloric acid and the solution evaporated to dryness it was recovered unaltered. The compound did not contain water of crystallization.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_{10}H_{14}O_2N_2S$.	Found. I.	II.
N	11.53	11.64	11.59

β-Hydroxypropylallylmalonic Acid, $CH_2:CH.CH_2$ / $CH_3.CH(OH)CH_2$ \> $C(COOH)_2$.—Two grams of the above thiourea were saponified by heating with 8 cc. of 50 per cent. potash for 2 hours at 130°–150°. Ammonia was observed when the tube was opened and hydrogen sulphide was evolved when the solution was acidified at a low termperature with hydrochloric acid. The malonic acid separated as an oil which we extracted with ether and dried over sodium sulphate. When the ether was evaporated at ordinary temperature the acid was obtained as a thick, viscous oil which soon crystallized in colorless rosettes of small prisms. It is very soluble in alcohol and hot benzene and insoluble in cold water. It melts at 120°–122° with effervescence. It gave no test for sulphur.

Silver Salt.—The acid dissolved immediately in dilute ammonia. On addition of an excess of silver nitrate the silver salt deposited and was washed with water and alcohol. It was dried over sulphuric acid. Silver determination:

I. 0.2623 gram substance gave 0.1379 gram Ag.

	Calculated for $C_9H_{12}O_5Ag_2$.	Found.
Ag	51.92	52.5

NEW HAVEN, CONN.,
Jan. 1, 1911.

[Contributions from the Sheffield Laboratory of Yale University.]

CXC.—ON HYDANTOINS: A SYNTHESIS OF PHENYLALANINE AND OF TYROSINE.

By Henry L. Wheeler and Charles Hoffman.

[FIRST PAPER.]

It has been known for a number of years that certain compounds containing the grouping —$HNCH_2CO$— are capable of condensing with aldehydes.

Plöchl,[1] applying Perkin's synthesis to hippuric acid, $C_6H_5CONHCH_2COOH$, found that it condenses with benzaldehyde and salicylaldehyde,[2] and Hofmann[3] showed that this acid condenses with pyruvic acid, but it was Erlenmeyer, Jr.,[4] who gave the correct explanation of the nature of the condensation products which are formed in these reactions. The latter also showed that hippuric acid condenses, in the presence of acetic anhydride and anhydrous sodium acetate, with a number of other aldehydes[5] and also with ethyl formate.[6] From these results and the fact that glycine,[7] H_2NCH_2COOH, was found to condense with aldehydes, Erlenmeyer developed his important syntheses of amino acids, notably tyrosine,[8] phenylalanine,[9] serine,[9] cystine,[9] leucine,[9] etc.

The preparation of tyrosine, which previously had been synthetically obtained only by a more laborious method,[10] was shortened to four operations as follows: The *p*-hydroxybenzaldehyde condensation product of hippuric acid, an azolactone (yield, 85 per cent.) was hydrolyzed to benzoylamino-*p*-hydroxycinnamic acid by warming with alkali, and this

[1] Ber. d. chem. Ges., **16,** 2815 (1883).

[2] Plöchl and Wolfrum: *Ibid.*, **18,** 1183 (1885).

[3] *Ibid.*, **19,** 2554 (1886).

[4] Ann. Chem. (Liebig), **271,** 137 (1892); **275,** 1 (1893). Erlenmeyer and Stadlin: *Ibid.*, **337,** 283, 265. Erlenmeyer and Arbenz: *Ibid.*, **337,** 302 (1904).

[5] Erlenmeyer: Ann. Chem. (Liebig), **307,** 70 (1899). Erlenmeyer, with Bade, Mattes, Stadlin and Wittenberg: *Ibid.*, **337,** 205, 222, 265, 271, 283, 294 (1904).

[6] Erlenmeyer and Stoop: *Ibid.*, **337,** 236.

[7] Ber. d. chem. Ges., **25,** 3445 (1892). Erlenmeyer and Früstuck: Ann. Chem. (Liebig), **284,** 36 (1895).

[8] Ber. d. chem. Ges., **30,** 2981 (1897). Erlenmeyer and Halsey: Ann. Chem. (Liebig), **307,** 138 (1899).

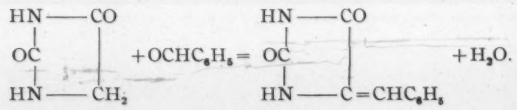
[9] With Kunlin: *Ibid.*, **307,** 146 (1899); **337,** 236; **316,** 145 (1901).

[10] Erlenmeyer and Lipp: *Ibid.*, **219,** 170 (1883).

in alkaline solution was reduced with sodium amalgam to benzoyltyrosine (yield, 10–15 per cent.), then on heating with hydrochloric acid, tyrosine hydrochloride was obtained (yield, 25 per cent.). The last two operations were later improved by Emil Fischer so that a yield of 65–70 per cent. of benzoyltyrosine was obtained, the benzoyl derivative being hydrolyzed almost quantitatively by boiling with hydrochloric acid.[1]

Erlenmeyer also showed that creatine, $H_2NC(NH)N(CH_3)CH_2COOH$, condenses with benzaldehyde, under the influence of acetic anhydride, giving benzalacetylcreatinine.[2] He then examined phenylglycine, acetylphenylglycine, and phenylhydantoin, but these substances did not condense with benzaldehyde by his method.[3]

With the intention of making a study of various hydantoin derivatives for synthetical purposes, we first examined the behavior of hydantoin itself when heated with aldehydes and we have found that excellent yields of condensation products are obtained when this substance is simply boiled with aldehydes in acetic acid solution and in the presence of anhydrous sodium acetate. The use of acetic anhydride is unnecessary. For example, with benzaldehyde benzalhydantoin is easily obtained in yields of 70–80 per cent. of the calculated. The reaction takes place as follows:



Benzalhydantoin has previously been obtained by a different method. Ruhemann and Cunnington[4] found that phenylpropiolic ester condenses with urea in the presence of sodium ethylate, and Ruhemann and Stapleton[5] showed that this

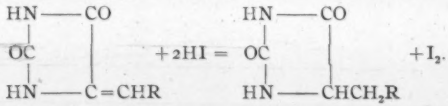
[1] Ber. d. chem. Ges., **32,** 3638 (1900).
[2] Ann. Chem. (Liebig), **284,** 49 (1895).
[3] *Ibid.*, **307,** 73 (1899).
[4] J. Chem. Soc., **75,** 958.
[5] *Ibid.*, **77,** 246 (1900).

product, first supposed to be the ureide of phenylpropiolic acid, is, in fact, benzalhydantoin.

We have also found that the condensation of hydantoin with anisaldehyde, *p*-nitrobenzaldehyde, furfural, piperonaldehyde, salicylaldehyde, and 3,5-dichlor-*p*-hydroxybenzaldehyde takes place in a similar manner to the above and that the yields are excellent.

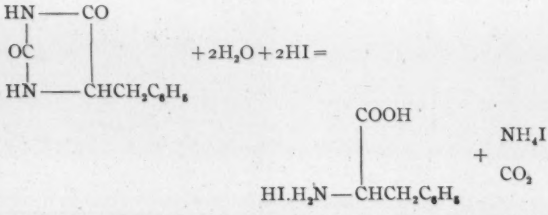
These condensation products would be of only secondary interest if it were not possible to smoothly reduce them to the corresponding hydrated hydantoins and then hydrolyze the products to the amino acids. These results have now been accomplished.

We find that the condensation products on moderate warming with hydriodic acid readily give the saturated hydantoins:



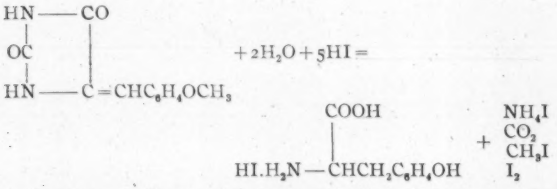
When anisalhydantoin is boiled for a short time with hydriodic acid, *p*-hydroxybenzalhydantoin or tyrosine hydantoin is almost quantitatively obtained.

When the action is more vigorous or when benzalhydantoin or, rather, benzylhydantoin is boiled for a number of hours with hydriodic acid and a little red phosphorus, it is smoothly converted into the hydriodic acid salt of phenylalanine.



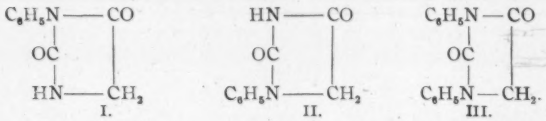
When anisalhydantoin is boiled with hydriodic acid of specific gravity 1.7, a little red phosphorus being added, four

steps are combined in one operation: A reduction of the double bond takes place, methyl iodide is evolved, the hydantoin ring is opened and finally the urea grouping undergoes hydrolysis and tyrosine can be practically quantitatively obtained. The reaction may be represented as follows:



These syntheses of tyrosine and phenylalanine require only two operations, in each case, starting with commercial material.

The tendency of *N*-substituted hydantoins to condense in the above manner with aldehydes has also been examined by us in the case of the following three types of phenylhydantoins:

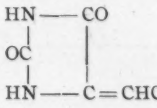


I. II. III.

1-Phenylhydantoin (I) condenses with anisaldehyde as readily as the unsubstituted hydantoin. On the other hand, under the same conditions, we obtained no condensation product with either 3-phenylhydantoin (II) or with 1, 3-diphenylhydantoin (III).

We intend later to give an account of the chemical behavior of hydantoin condensation products and the employment of hydantoins in other syntheses.

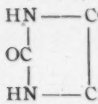
EXPERIMENTAL PART.

Benzalhydantoin,  .—Ten grams of hydan-

toin, 20 grams of fused sodium acetate, 40 cc. of glacial acetic acid, 10 drops of acetic anhydride and 15 grams of benzaldehyde were mixed and boiled in an oil bath for 3 hours. The reaction was probably complete in much less time. After cooling, water was added to the mixture until no further precipitation occurred. The yellow substance which separated was filtered, washed with water, and dried. It weighed 15.1 grams, or 80 per cent. of the calculated. A duplicate experiment gave a yield of 70 per cent. of the calculated, while another experiment, performed as above, with the exception that only ten grams of fused sodium acetate were used, gave only a 56 per cent. yield of benzalhydantoin. When the condensation product was crystallized from alcohol it gave straw-yellow needles melting at 220°. It agreed with the description of benzalhydantoin given by Ruhemann.[1]

	Calculated for $C_{10}H_8O_2N_2$.	Found.
N	14.89	14.68

4-Benzylhydantoin (Phenylalaninehydantoin),



.—Ten grams of benzalhydantoin, 3 grams of red phosphorus and 45 cc. of hydriodic acid of specific gravity about 1.7 were boiled for 45 minutes, the heating being done in an oil bath. The hydriodic acid was then evaporated and the residue was boiled with water and filtered from the excess of red phosphorus. On concentrating the solution 7.4 grams of benzylhydantoin, melting to an oil at 188°–190°, were obtained.

From the mother liquor, after removing the phosphoric acid with barium hydroxide, and the excess of barium by carefully precipitating with sulphuric acid, 1.6 grams of phenylalanine were found to have been formed under the above conditions. 4-Benzylhydantoin crystallizes from alcohol in colorless, flat, lancet-shaped crystals. On slowly cooling it forms

[1] *Loc. cit.*

prisms. It also crystallizes readily from water and melts at 190° to a clear oil.

	Calculated for $C_{10}H_{12}O_2N_2$.	Found.
N	14.73	14.40

We also obtained this compound when equal weights of potassium cyanate and phenylalanine were dissolved in water, evaporated to a syrup, and the residue warmed with dilute hydrochloric acid. The product melted at 190° without effervescence.

Reduction of Benzalhydantoin with Aluminium Amalgam.—The reduction by this method was not as satisfactory as that by hydriodic acid, owing to the formation of an aluminium compound. Seven and six-tenths grams of benzalhydantoin were dissolved in 100 cc. of water containing 4.5 grams of potassium hydroxide, and aluminium amalgam, prepared from 4 grams of aluminium, was added. Hydrogen was evolved for 3 hours before all the aluminium was used up. The mixture was then boiled and filtered and the warm filtrate was acidified with hydrochloric acid. A flocculent precipitate separated which weighed 4.1 grams. This had no definite melting point, contained aluminium, and could not be crystallized from any solvent. The analytical results were as follows:

	Calculated for $C_{10}H_{12}O_2N_2.3Al(OH)_3$.	Found.
N	6.33	6.45
Al	18.32	17.50

From the filtrate 5 grams of crystalline material were obtained. This proved to be a mixture of benzylhydantoin and benzylhydantoic acid. Upon crystallizing from alcohol the hydantoic acid separated, and on evaporating the filtrate the hydantoin was obtained.

4-Benzylhydantoic Acid (*α-Ureido-β-phenylpropionic Acid*), $H_2NCONHCH(COOH)CH_2C_6H_5$.—This substance was obtained when the above hydantoin was boiled for a few minutes with dilute sodium hydroxide and then precipitated in the cold with dilute hydrochloric acid. It crystallizes from alcohol in color-

less prisms and it melts at the same temperature as the hydantoin, namely, at 190°; it is readily distinguishd from this substance, however, by melting with vigorous effervescence.

	Calculated for $C_{10}H_{12}O_3N_2$.	Found.
N	13.46	13.00

This compound has recently been shown to be formed in the animal body when phenylalanine is injected into the femoral vein of cats.[1] Our material thoroughly agrees with Dakin's description of the substance. We may add that on warming this substance with dilute hydrochloric acid it is converted into the hydantoin.

Action of Hydriodic Acid on 4-Benzylhydantoin.

Preparation of Phenylalanine.—Five grams of benzylhydantoin, 1.5 grams of red phosphorus, 25 cc. of hydriodic acid (specific gravity 1.7) and 6.8 grams of iodine were boiled for five hours in a flask attached to a return condenser.

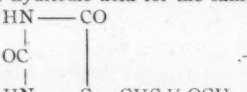
On evaporating the hydriodic acid and extracting the residue with boiling water and concentrating, 1.2 grams of unaltered benzylhydantoin separated. The filtrate gave, on precipitating with ammonia, 2.1 grams of phenylalanine, melting with effervescence at 262°, and from the mother liquor after removing the phosphoric acid and ammonia with barium hydroxide, 1 gram more of phenylalanine was obtained. In this case 24 per cent. of the original material was recovered unaltered and 71 per cent. was converted into phenylalanine.

	Calculated for $C_9H_{11}O_2N$.	Found.
N	8.48	8.78

Action of Barium Hydroxide on 4-Benzylhydantoin.—Five grams of benzylhydantoin, 33 grams of crystallized barium hydroxide, and 30 cc. of water were boiled for 5 hours in a hard-glass flask attached to a return condenser. Barium carbonate soon separated and ammonia was given off. After extracting the contents of the flask with boiling water and

[1] Dakin: J. Biol. Chem., **6**, 241 (1909).

removing the barium by means of carbon dioxide, the solution was concentrated to a volume of about 75 cc. Then, on acidifying with acetic acid and allowing the solution to stand, 1.3 grams of benzylhydantoic acid separated. The mother liquor was concentrated to a small volume and 3.2 grams of phenylalanine were obtained. In this experiment 23.7 per cent. of the benzylhydantoin was converted into the hydantoic acid and 73 per cent. into phenylalanine. The result, in regard to the preparation of phenylalanine, is practically identical with that obtained on boiling the hydantoin with a saturated solution of hydriodic acid for the same time.

Anisalhydantoin,  .—Ten grams of hydantoin, 20 grams of fused sodium acetate, 40 cc. of glacial acetic acid and 16 grams of freshly distilled anisaldehyde (calculated, 13.6 grams) were mixed in a flask attached to a return condenser and boiled for 2 hours. After cooling, water was added and the product that separated, consisting of almost pure anisalhydantoin, was washed and dried. It weighed 15 grams and with the 0.4 gram obtained from the mother liquor, on concentrating, the yield was 71.5 per cent. of the calculated. Three other experiments, as above, gave 74, 70 and 72 per cent. yields. Varying the time of heating beyond 2 hours and increasing the amount of sodium acetate did not increase the yield.

On evaporating the acetic acid solutions and washings from the crude product with hydrochloric acid, unaltered hydantoin could invariably be extracted with alcohol. In one experiment, therefore, we increased the amount of anisaldehyde to twice the weight of hydantoin employed; the yield was then 69 per cent. of the calculated. Another experiment was performed as above, only that one molecular proportion of acetic anhydride was added. The yield of material then, on adding water, was 64 per cent. and from the mother liquor 12 per cent. more of less pure material was obtained on evaporating the acetic acid.

Attempts to effect a condensation by warming the hydantoin with anisaldehyde in glacial acetic acid or in acetic anhydride, without sodium acetate, gave very little condensation product and the yield was poor when less than two parts by weight (compared to the weight of hydantoin), of fused sodium acetate was used.

Anisalhydantoin is difficultly soluble in boiling water, only moderately soluble in alcohol, and readily soluble in glacial acetic acid. It crystallizes from alcohol in brownish yellow prisms which melt at 243°–244° wth slight effervescence. It dissolves in cold alkali and is precipitated unaltered by acetic or hydrochloric acid; when it is boiled with alkali it gives *p*-methoxyphenylpyruvic acid.

	Calculated for $C_{11}H_{10}O_3N_2$.	Found.
N	12.84	12.63

Bromanisylhydantoin, $C_{11}H_9O_3N_2Br$.—Two grams of anisalhydantoin were suspended in 30 cc. of glacial acetic acid and 1.5 grams of bromine (calculated for 2 atoms) were slowly added. Heat was evolved and the hydantoin went into solution. There was no evidence of hydrobromic acid being liberated until the solution was warmed. The solution was evaporated to dryness on the steam bath, the residue treated with water, washed and dried. It weighed 2.7 grams, which is almost the calculated for a monobrom compound. It is difficultly soluble in water and only moderately soluble in alcohol, from which it crystallizes in clusters of long, light-yellow needles. It melts to an oil at 247°. When gently warmed with an aqueous solution of silver nitrate and nitric acid silver bromide separates.

	Calculated for $C_{11}H_9O_3N_2Br$.	Found.
N	9.43	9.40

Preparation of Tyrosine.—Five grams of anisalhydantoin, 2 grams of red phosphorus and 25 cc. of hydriodic acid (specific gravity 1.7) were boiled in a flask attached to a return condenser for 4 hours and then 6.8 grams of iodine (calculated

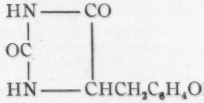
for 2 atoms) were added and the boiling continued for 5 hours longer. Iodine vapors were immediately evolved and methyl iodide was noticed in the condenser. After the iodine had disappeared, the methyl iodide was allowed to escape by momentarily disconnecting the condenser. When the heating was discontinued the hydriodic acid was evaporated and the residue was extracted with hot water. On concentrating and cooling no hydantoin separated. The solution was then made alkaline with ammonia and 3.5 grams of tyrosine, melting at about 295°, separated. After the removal of phosphoric acid from the mother liquor by means of barium hydroxide and of the excess of the latter with carbon dioxide and a drop of sulphuric acid, and evaporating, 0.2 gram more tyrosine was obtained. The yield was 89.1 per cent. of the calculated.

	Calculated for $C_9H_{11}O_3N$.	Found.
N	7.73	7.97

In another experiment 5 grams of anisalhydantoin were boiled with 25 cc. of hydriodic acid (specific gravity 1.7) and 1.5 grams of red phosphorus for 6 hours. After evaporating the acid and proceeding as above 1 gram of tyrosinehydantoin separated from the aqueous solution, and from the mother liquor 3.15 grams of tyrosine were obtained. In this experiment 76 per cent. of the material was converted into tyrosine and 20 per cent. into tyrosinehydantoin.

In regard to the melting point, or rather decomposition point, of synthetic tyrosine we wish to state that it is indefinite. On rapidly heating in one case the substance effervesced at 340°, while the other portion of the same preparation melted at 295° when kept in a bath at this temperature for about a minute.

4-p-Hydroxybenzylhydantoin (*Tyrosinehydantoin*),



.—Seven and seven-tenths grams of

anisalhydantoin, a little red phosphorus and 35 cc. of hydriodic acid (specific gravity 1.7) were boiled for one hour and then 20 cc. of glacial acetic acid were added. On warming again all the organic material dissolved. The acid was evaporated and the residue was extracted first with boiling water and finally with a little dilute ammonia. On evaporating, 5.7 grams of crystalline material separated, or 79.1 per cent. of the calculated for tyrosine hydantoin. The filtrate gave 0.5 gram more substance, which proved to be tyrosine when it was evaporated to dryness, the residue taken up in a little water, ammonia added, evaporated to dryness again, and the residue treated with dilute acetic acid. Under these conditions 7.8 per cent. of the calculated for tyrosine was obtained.

In another experiment, using the same amount of hydriodic acid, one-half the amount of anisalhydantoin and heating for the same time, the percentage yield of tyrosinehydantoin was about the same, namely, 83 per cent. of the calculated.

Tyrosinehydantoin crystallizes from water in beautiful, small, colorless prisms. It appears to be a little less soluble in alcohol and it melts at 257°–258° to an oil which at first slightly effervesces, then decomposes. It dissolves in alkali and ammonia and it is precipitated by acetic acid as well as hydrochloric acid. It gives an intense Millon reaction.

	Calculated for $C_{10}H_{10}O_3N_2$.	Found.
N	13.59	13.59

Blendermann[1] isolated from the urine of rabbits fed with tyrosine a substance which agreed in analytical results with those calculated for tyrosinehydantoin. The substance, on hydrolysis with baryta, gave tyrosine. Blendermann's substance, however, does not agree in its properties with our tyrosinehydantoin. He describes the substance as crystallizing in yellow needles which, on heating, turn brown at about 270° and then melt at 275°–280°, or 18°–23° higher than our material. It is possible that these differences may

[1] J. Physiol. Chem., **6**, 253 (1882).

be due to Blendermann's hydantoin being an optically active isomer.

4-p-Hydroxybenzylhydantoic Acid (*Tyrosinehydantoic Acid*), $H_2NCONHCH(COOH)CH_2C_6H_4OH$.—The hydrolysis of tyrosinehydantoin to the hydantoic acid does not take place as easily or as smoothly as the corresponding reaction in the case of phenylalaninehydantoin and the conditions of solubility are the reverse. In this case the hydantoic acid is more soluble than the hydantoin. It can be prepared by boiling the hydantoin with dilute alkali for a short time. Some ammonia is evolved and on acidifying with acetic acid the unaltered hydantoin is precipitated. On evaporating the filtrate to dryness and acidifying the residue with dilute hydrochloric acid the hydantoic acid is obtained.

Tyrosinehydantoic acid is best prepared from tyrosine and potassium cyanate. This method has previously been used by Jaffe,[1] but, owing either to this method of isolating the substance or to having used impure tyrosine, he obtained an impure product.

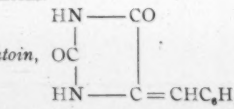
Synthetic tyrosine was dissolved in hot water and treated with an equal weight of potassium cyanate in a small amount of water. The solution was then concentrated (to 10 cc. for 1 gram of tyrosine) and hydrochloric acid was added at ordinary temperature. On standing overnight prisms separated which melted with effervescence at 172°. The material was readily soluble in alcohol and water and on recrystallizing the melting point was not changed. When boiled with dilute hydrochloric acid it gives tyrosinehydantoin, melting at 257°–258°.

	Calculated for $C_{10}H_{12}O_4N_2$.	Found.
N	12.50	12.40

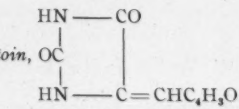
Action of Barium Hydroxide on Tyrosinehydantoin.—Four and eight-tenths grams of tyrosinehydantoin, 30 grams of crystalllized barium hydroxide and 30 cc. of water were placed in a flask attached to a return condenser and boiled for 6 hours. The mixture was diluted with water, filtered hot from

[1] Z. physiol. Chem., 7, 310 (1882).

the barium carbonate that had been formed, carbon dioxide was passed into the solution, and the solution filtered again and concentrated. On adding acetic acid a snow-white mass of long, slender, silky needles separated. The first crop weighed 2.0 grams and on concentrating 1.35 grams more were obtained. This material melted with effervescence when kept at 295° and proved to be tyrosine. The syrupy mother liquor and the barium carbonate precipitates were dissolved in acetic acid and the barium precipitated by a slight excess of sulphuric acid. On concentrating this solution, finally adding ammonia and acetic acid, 0.7 gram of material separated which, on crystallizing from water, melted at 255° with effervescence and was therefore unaltered hydantoin. The yields were 79.6 per cent. of the calculated of tyrosine and 14.5 per cent. of hydantoin.

Piperonalhydantoin,  .—Five grams of hydantoin, 8.5 grams piperonal (calculated, 7.5 grams), 20 cc. of glacial acetic acid and 10 grams of fused sodium acetate were boiled, without the addition of acetic anhydride, for 2 hours. On cooling and adding water 10 grams of condensation product were obtained, or 86 per cent. of the calculated. This material was fairly soluble in alcohol and dilute acetic acid and it crystallized in clusters of yellow prisms melting at 245°. It is readily soluble in glacial acetic acid.

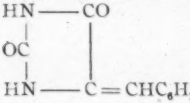
	Calculated for $C_{11}H_8O_4N_2$.	Found.
N	1207	11.85

Furfuralhydantoin,  .—Five grams of hydantoin, 10 grams of fused sodium acetate, 6 grams of furfuraldehyde (calculated, 4.8 grams), 20 cc. of glacial acetic acid and no acetic anhydride, were mixed and boiled for 1

hour and 15 minutes. The product, on washing with water and drying, weighed 6.8 grams, or 76 per cent. of the calculated. This was first crystallized from dilute acetic acid and then from alcohol. It formed dark yellow prisms which melted to a dark oil at 232°. When dissolved in concentrated sulphuric acid it gave an intense green color.

	Calculated for $C_6H_6O_3N_2$.	Found.
N	15.73	15.77

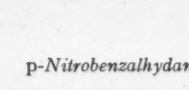
3,5-Dichlor-p-*hydroxybenzalhydantoin*,



.—Thirteen and two-tenths grams 3,5-dichlor-*p*-hydroxybenzaldehyde,[1] 7.5 grams of hydantoin, 15 grams of fused sodium acetate and 35 cc. of glacial acetic acid were boiled for 3.5 hours without the addition of acetic anhydride to the mixture. In two hours a cake of solid material had separated from the hot acetic acid. The contents of the flask, on treating in the usual manner, gave 13.8 grams of condensation product, while the calculated is 18.8 grams. It was every difficultly soluble in alcohol and almost insoluble in boiling water. For analysis it was crystallized from a mixture of acetic acid and alcohol, clusters of light yellow, long, slender needles being obtained. These melted either directly at 300°, with effervescence, or on keeping the substance at this temperature for a short time. It gives an orange ammonium salt, which is difficultly soluble in water. It dissolves readily in alkali.

	Calculated for $C_{10}H_6O_3N_2Cl_2$.	Found.
N	10.25	10.04

p-*Nitrobenzalhydantoin*,



.—Two parts

[1] Auwers and Reis: Ber. d. chem. Ges., **29**, 2356 (1896).

of hydantoin, 3 parts of *p*-nitrobenzaldehyde, 3 parts of fused sodium acetate, and 5 parts of glacial acetic acid were mixed and boiled for 1 hour. The condensation product separated as a cake from the hot solution. It was boiled with water and then found to be very slightly soluble in organic solvents. It was crystallized from a large volume of water for analysis, whereupon it formed lemon-yellow prisms melting at 254° with decomposition.

	Calculated for $C_{10}H_7O_4N_3$.	Found.
N	18.02	17.85

When this hydantoin is dissolved in normal potassium hydroxide it gives a blood-red solution.

1-Phenylanisalhydantoin, $C_6H_5N(CO)(OC)(HN)C=CHC_6H_4OCH_3$.

Five grams of 1-phenylhydantoin, 6 grams anisaldehyde (calculated, 4 grams), 10 grams of fused sodium acetate, 20 cc. of glacial acetic acid and a few drops of acetic anhydride were mixed and boiled for 2.5 hours. On treating in the usual manner 6.7 grams of condensation product were obtained, or 80 per cent. of the calculated. It was almost insoluble in hot water and difficultly soluble in alcohol. It crystallized from the latter solvent in small, yellow prisms, which melted to a brown oil at 251° without decomposition. On cooling and heating again it remelted at the same temperature.

	Calculated for $C_{17}H_{14}O_2N_2$.	Found.
N	9.52	9.67

When 3-phenylhydantoin and 1,3-diphenylhydantoin were treated precisely as in the above case nothing but unaltered material was obtained.

3-Phenylhydantoin was prepared from chloracetylurethane and aniline according to the directions of Frerichs and Beckurts.[1] 1,3-Diphenylhydantoin was obtained by a new method.

[1] Arch. Pharm., **237**, 337.

Phenyl isocyanate was mixed with phenylglycine in approximately molecular proportions, when on gently warming a reaction suddenly started that required cooling. The product was dissolved by warming with dilute alkali, filtered from some insoluble material, and precipitated by hydrochloric acid. This apparently gave the hydantoic acid melting at 195° with effervescence. When this was dissolved in hot alcohol with the addition of a little hydrochloric acid and allowed to crystallize, the diphenylhydantoin described by Bischoff and Hansdörfer[1] was obtained. It formed almost colorless plates melting at 137°. The plates or spangles had the striking property of reflecting all colors of the rainbow on separating from an alcoholic solution.

NEW HAVEN, CONN.,
December, 1910.

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[2]

PART III. THE REGULATION OF TEMPERATURE.

BY H. N. MORSE, W. W. HOLLAND, AND E. G. ZIES.

When the last work at 0° was done in 1906–1907,[3] the low temperature was secured by pumping water continuously over broken ice and around the metallic cans in which the cells were located. The temperature which was obtained in this way was not 0°, but was always somewhat higher. As a rule, it varied between 0°.15 and 0°.30. The maximum variation from the beginning of the work to the end was between 0°.12 and 0°.38. The temperature in the air space above the cells in which the manometers were located was always higher and much more variable. Such fluctuations in temperature are capable of producing very large *thermometer effects*. It was, therefore, determined, before beginning the

[1] Ber. d. chem. Ges., **25**, 2274 (1892).

[2] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers which have preceded the present one will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 137; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 257; **45**, 91 and 237.

[3] THIS JOURNAL, **37**, 425.

more elaborate attempts to ascertain the relation of osmotic pressure to temperature, to devise, if possible, some means of maintaining the cells *at o°* as exactly and continuously as we were able to maintain them at any higher temperature. The arrangement which was finally evolved for the purpose is shown in Figs. I, II and III. The apparatus, which is made of galvanized iron, consists of three principal parts: First, a can *A*, in which the cells are placed; second, a much larger one *B*, in which *A* is suspended by means of the arrangement shown in Fig. II; and third, the cylinder *C*, which shuts down tightly upon *B*. There is an enclosed chamber, *e*, running through the whole length of *C* and open at both ends, in which are located the upper ends of the manometers, and the two thermometers which are shown in the figure. The thermometers and manometers are exposed to view, when a reading is to be made, by opening the felt-lined door, *f*. In order that the door may be opened and closed from the outside, the detachable rod, *g*, by which the door is opened and shut, is made to extend through the top of the larger bath which surrounds *A*, *B* and *C*. The bottoms of both *A* and *B* are perforated, so that no water can collect in the cans.

The "larger bath," referred to above, is one of those ordinarily used for the measurement of pressure at higher temperatures. To prepare it for work at o°, it is emptied, and the circulating pipes, including the pump, are removed, leaving the copper-lined tank entirely empty. On the bottom of this, in the center, is placed a staging about 5 cm. high, on which rests the ice-filled arrangement consisting of *A*, *B* and *C*. All the space in the tank which is not occupied by *A*, *B* and *C* is filled with closely packed broken ice, and the water which collects upon the bottom is removed by means of an automatic siphon. All the space in the upper part of the bath—usually designated as the "air space"— which is not occupied by the upper part of *C* is filled with ice containers of such form that *C* is surrounded by them, except in front of the door, *f*. One of these occupies the space between the upper end of *C* and the top of the outer bath, the upper end of the chamber *e* being covered to prevent the entrance of water.

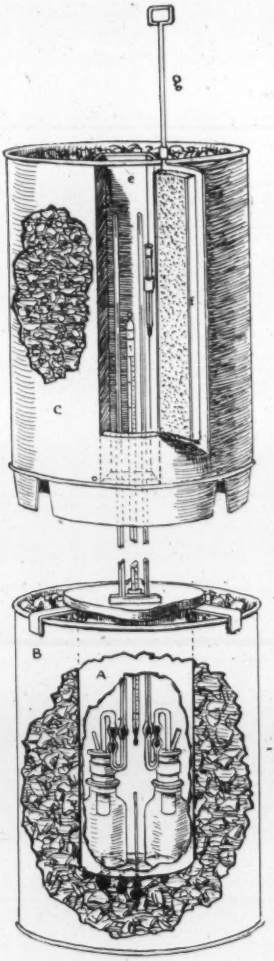


Fig. I.

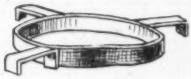


Fig. II.

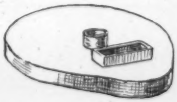


Fig. III.

All the ice containers in the air space above are open at the lower end, so that the broken ice moves constantly downwards as it melts away underneath, keeping the tank below and also the can *B* always full. A little over 300 kilograms of ice are required to fill the bath properly, and the amount of fresh ice which it is necessary to introduce at the top daily is between 20 and 25 kilograms.

The ice container above *C* and *C* itself, after picking out the ice in them, can be lifted through the opened top of the bath, whenever cells are to be removed from *A*. If cells are to be introduced, all parts of the bath except *C* and the containers above it are closely packed with ice, and, after waiting until the temperature in *A* has fallen to 0°, the cells are placed in position. *C* is brought down upon *B* and packed with ice. Finally, the container which belongs directly above *C* is placed in position and filled with ice.

The arrangement described above served its purpose perfectly. The temperature in *A* did not deviate sensibly from 0° during the entire work, and for the first and the last time, we were nearly free from *thermometer effects*. The temperature in the manometer space, *e*, was less satisfactory. It appeared to vary from 0° to 0°.3, but this is believed to have been due to the lamp which was used in reading, more than to any inability on the part of the arrangements to maintain a temperature of zero in the space occupied by the manometers. We had not then adopted the plan of screening the light with a solution of nickel sulphate, which was afterwards found to reduce the heating effects of the lamp by about 99 per cent.

The complete system for the regulation of temperatures above 0° is shown in Fig. IV. It consists of a relay, *R*; two condensers of large capacity, *C* and C_1; a stove, *s*; a thermostat, *T*; a single battery cell, *B*; and two lamps, *l* and l_1. The different parts can, of course, have any convenient location whatever. The stove circuit (110 volts) begins at the point marked +, passes through the binding posts of the "local" on the relay, thence through the stove and out again. If the circuit is broken between the binding posts, the current

passes through the lamp, *l*, thence through the stove and out. In other words, the breaking of the circuit between the relay posts throws the lamp into series with the stove, cutting down the current. All sparking between the platinum points of the relay is prevented by the condenser *C*, which is likewise discharged through the lamp *l*.

The circuit from the battery, *B*, leaving from the point marked +, passes around one side of the condenser, *C*, through the "main line" posts of the relay, *R*, to the other side of the condenser, *C*, thence through the thermostat, *T*, back to the battery. Sparking in the thermostat is prevented by the condenser, *C*. In this system some current passes through the stove all of the time, but the amount which may pass, when the relay circuit is open, can be regulated within wide limits by a proper selection of lamps for the socket, *l*.

It has been stated elsewhere that we use lamps as stoves, for the reason that they heat up and cool down more quickly, and are more convenient, than other electrical heating devices. But we use no lamps of over 50 candle power. If a temperature much above that of the air is to be maintained, the greater part of the heating is done by gas burners or stoves, only so much of the work being left to the electrical devices as may be necessary for purposes of regulation.

The elaboration of the general scheme to which all of the baths now conform was well advanced when the present work was taken up, and we were able at the close of 1908[1] to state the principle on which they are constructed and to illustrate its application to one type of bath. Since then, it has been applied in every detail to two other types of bath. The principle in question was stated as follows: *"If the water in any bath is made to pass rapidly (1) over a continuously cooled surface, then (2) over a heated surface which is more efficient, but which is under the control of a thermostat, and (3) again over the cooling surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set; and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the*

[1] This Journal, **41**, 106.

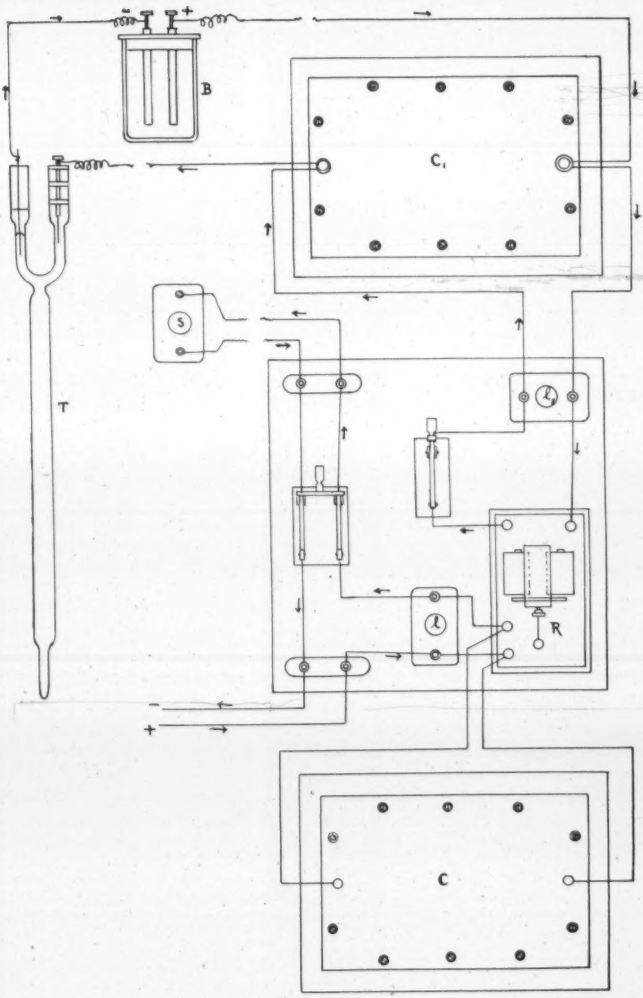


Fig. IV.

water. The principle is a general one and provides for the maintenance of any temperature between 0° and the boiling point of water. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid either in the work of the cooling surface or in that of the heating surface."

The three types of baths in use are (1) the baths for general purposes, which are employed intermittently, as occasion arises; (2) those in which the membranes are deposited, and the solutions are maintained at constant temperature, which are always "at temperature" while the work is in progress; and (3) the baths in which osmotic pressure is measured, which are also always "at temperature." The first type has been explained in an earlier paper, but not the other two. Types II and III will, however, be more readily understood if the description of them is preceded by a brief account of type I. For this reason, and for the sake of completeness, we shall venture to reproduce some of the figures which appeared in the earlier paper, and to repeat some of the explanations which accompanied them.

Type I.

The various parts of the bath which was first developed on the principle previously stated, are shown in Figs. V to XI, inclusive. "Fig. V represents a cross section of a galvanized iron bath holding about 60 liters. It rests upon the wooden base *a a*, which is raised above the table by the blocks and rubber pieces *b b*, and is surrounded by the thick hair-pad *c c*. Inverted over a hole in the center, and riveted and soldered to the bottom of the bath, is the cylinder *d d d*, which serves as a receptacle for the lamp *e*, or any other suitable kind of electrical heating device. The hole in the wooden base, *a a*, is slightly larger than in the bottom of the bath, and into this is fitted the block *f*, on which is fastened the lamp base, *g*, and the lamp guard, *h h*. The lamp block is held in its place by buttons screwed to the bottom of the wooden base.

"Resting upon the framework, *i i* (Fig. V) and *i i i* (Fig. VI), is the continuous block-tin pipe, *j j j j*, through which the hydrant water circulates. This furnishes the 'cooling surface' previously referred to. The running water enters the bath at *k* and leaves it at *l*. The course of the water in the pipe, after entering the bath, is continuously horizontal or upward—never downward. This arrangement is necessary in order to prevent the lodgment of air in any part of the pipe. The plan of the continuous tin pipe and of the frame on which it rests is seen in Fig. VI. The successive coils of the pipe (six in number) are separated by the pegs seen in Figs. V and VI, and on these rests the galvanized iron disc *m m*. The hood *n n* shuts down tightly over a flange on the disc, *m m*, and is secured in its place by means of set screws directed towards *d d*. The form of the hood will be clear from the figure, and it is necessary only to call attention to the pin holes, for the escape of air, at *o o*, and to the larger holes at *p p*, through which a portion of the water raised by the propeller, *r*, escapes into the outer bath.

"The propeller, *r*, is revolved at any required speed by a smooth porpoise-hide belt, six mm. in width, which is passed around the pulley *s*, and over the pulley of a small motor located at some distance from the bath. The thermostat is seen at *u*, and the thermometer at *v*. The supports for both are clamped to the rim of the bath, as is also the adjustable support, *w w*, for the propeller and its accessories.

"It is quite essential that the hydrant water flowing through the pipe in the bath shall be under a constant pressure, otherwise much water and heat are necessarily wasted. The arrangement by which the constant pressure is secured is shown in Fig. VII. It consists of a large standpipe *a* with an overflow *b* near the top. The water from the tap enters at the bottom and passes to the bath through *c*, where the flow is controlled by a stopcock. The circulating water is thus brought under an invariable pressure and it is possible to regulate the quantity passing through the bath with great exactness and for long periods.

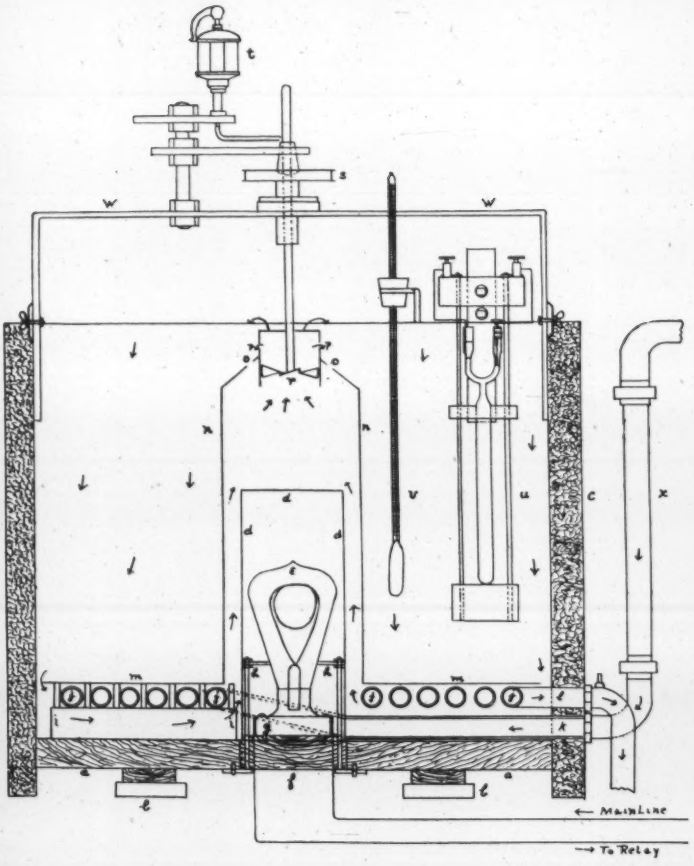


Fig V

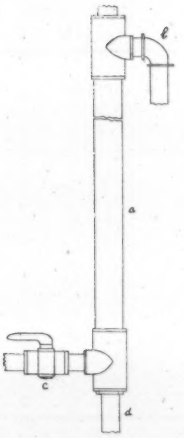


Fig. VII.

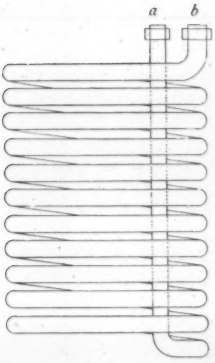


Fig. VIII.

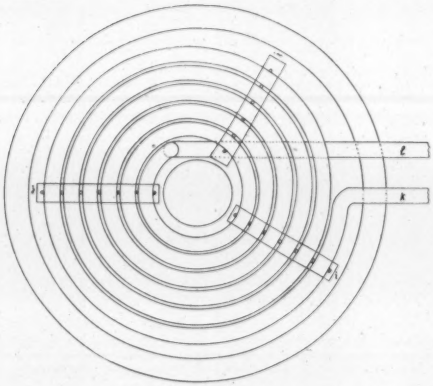


Fig. VI.

"It frequently happens that the temperature of the hydrant water is higher than that at which it is desired to maintain the bath. In such cases, the section of pipe *x*, Fig. V, is removed and replaced by another leading to the coil of block-tin pipe seen in Fig. VIII. The water enters the coil at *a* (Fig. VIII) and passes out of it at *b* into the bath. To cool the hydrant water before it enters the bath, the large and well-protected box in which the coil is located is filled with ice. With the aid of the coil, surrounded by ice, it is practicable to maintain quite low temperatures in the warmest weather.

"It remains to explain the electrical arrangements for heating the water in the bath. It is important that the metallic surface, *d d d* (Fig. V), over which the water passes in its upward course through the hood, shall be quickly heated and readily cooled; hence all unnecessary material in the space heated by the stove is to be avoided, and the stove itself should be of the lightest kind. For this reason, lamps have been preferred to any other variety of electrical heating device. Another great advantage to be gained by the use of lamps is the ease with which, by the selection of lamps with different candle power, the capacity of the stove is suited to the work to be done, i. e., to the temperature to be maintained in the bath.

"The arrangement for the regulation of the heater (*e*, Fig. V) by the thermostat (*u*, Fig. V) is shown in Fig. IX.

"The thermostat is shown separately in Fig. X. The tube containing the mercury is made larger or smaller, according to the degree of sensitiveness which is required of the instrument. It is also drawn out at the lower end into a smaller tube, which may be broken off and afterwards resealed if it becomes necessary to remove the mercury and cleanse the glass. The narrow tubes in the upper part of the instrument are also varied in diameter according to the requirements of the work. The instrument is filled with mercury until it enters the widened portion of the two tubes at the top. The end of a platinum wire is buried to a considerable depth in the mercury in one tube, and on the top of the mercury a quan-

tity of dry shellac is placed. The shellac is melted, and diminished pressure is applied at the other outlet until the mercury, followed by the molten shellac, recedes well into the narrower portion of the tube, when the shellac is allowed to cool and solidify. The other tube at the top is provided with an adjustable platinum wire, the function of which is sufficiently obvious.

"A thermostat of the form just described has the advantage that all of the mercury in the instrument can be submerged in the water of the bath, while the arrangement for adjustment remains above the surface of the water. But the range of temperatures through which it can be used with a fixed quantity of mercury is small. That is, the quantity of mercury must be regulated with reference to the temperature which is to be maintained. This, however, gives very little trouble. If a thermostat is to be employed to maintain a bath at some particular temperature, e. g., 25°, it is plunged—after removing the adjusting screw—into a bath having a slightly higher temperature, and whatever mercury ascends into the wider portions of the tube is removed by means of a very fine pipette. On the other hand, if the mercury recedes too far into the narrow tube, more is added.

"Fig. XI represents the support for flasks, etc., which is used in the bath. It is clamped to the rim of the bath, and, as will be seen from the figure, it can be depressed to any required depth in the water. The bottom is perforated to permit the rapid passage of water. Each bath of the size represented in Fig. V will accommodate five such supports in addition to the thermostat and thermometer.

"The use of the bath is very simple. The thermostat is adjusted to close the circuit at the temperature at which the bath is to be maintained. The bath is brought nearly to that temperature by means of hot water, or ice, or by passing a current of hydrant water through the coiled pipe in the bottom. The flow of hydrant water—cooled, if necessary, by first passing it through the ice coils (Fig. VIII)—is then so regulated that it will very slowly lower the temperature of the circulating water in the bath. The rate of the lower-

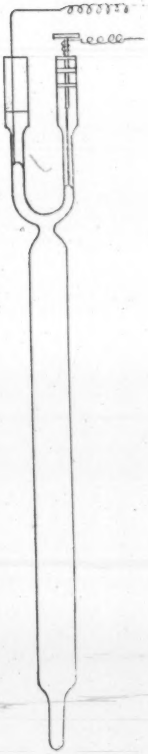


Fig. X.

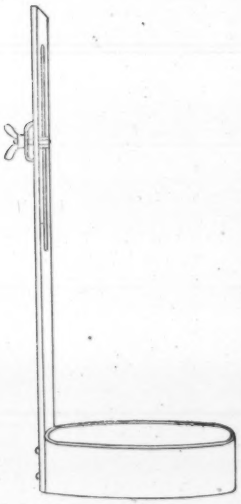


Fig. XI.

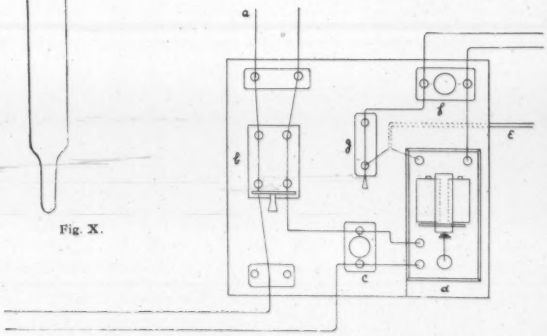


Fig IX.

ing need not exceed 0°.25 per hour, and it should be, for reasons of economy, as small as it is possible to make it. The lamp which is employed as a heater is selected with reference to the temperature to be maintained. It is only necessary that it shall be able, by burning all the time, to raise the temperature of the bath somewhat faster than the running hydrant water is able to lower it. The thermostat will then permit the lamp to burn only as much of the time as is necessary to maintain the temperature for which the instrument is set.

"The water, as it reaches the top of the hood, after passing over the heating surface, is symmetrically distributed towards all sides of the bath, giving a uniformity of temperature throughout the bath which is very satisfactory.

"The maintenance of any temperature from a little above 0° to that of the room can be readily accomplished by means of the hydrant water, with or without ice. If, however, a temperature above that of the room is to be maintained, the flow of the hydrant water is cut off. The outer surface of the bath and the free surface of the water then becomes the 'cooled' surface, and the bath works on precisely the same principle as when hydrant water is made to circulate through the tin pipe in the bottom. If a temperature above 50° is to be maintained, the consumption of electrical energy becomes expensive in large baths, and it is well to accomplish a portion of the heating by other means. This is done in various ways, the simplest of which is to remove the wooden base and place a gas stove under the bath, taking care so to regulate the quantity of burning gas that the stove *alone* cannot raise the temperature of the bath to the required height. It is only the remainder of the work which is then accomplished by the electrical heater. Another method of economizing electrical energy, when high temperatures are to be maintained, is to cause hot water to circulate through the pipe in the bottom of the bath."

Type II.

Fig. XII represents one of the baths in which the membranes are deposited, and the cells and solutions are main-

tained at constant temperature. The "*cooled surface*" is furnished by the 8 brass pipes, 1 to 8. The hydrant water, cooled by ice if necessary, enters pipe 1 at the end of the bath and leaves by pipe 8, circulating through the others in the order in which they are numbered. For all temperatures below the highest temperature of the room, it is necessary to keep some cold water in circulation through this system of pipes. The amount which is sent through will, of course, depend on the difference between the temperature of the hydrant water and that which is to be maintained in the bath. It is only necessary that the cooling surface shall be capable of carrying the temperature of the bath a *very little* below that which is to be maintained. Any larger consumption of the hydrant water is useless and wasteful of heat. The external arrangements are precisely like those of baths of type I. If the hydrant water is to be cooled before entering the bath, as when a low temperature, e. g., 5°, is to be maintained in summer, it is passed through the coil shown in Fig. VIII, which is surrounded by ice. The arrangement shown in Fig. VII is also employed to secure a constant pressure upon the circulating water. A word of caution regarding the valves to be used, when a constant pressure is to be maintained, may be of use to others. All of our pressure arrangements were constructed, in the first instance, in accordance with correct principles, so far as we knew; but it was found that they *would not* maintain constant pressure. The flow of water diminished continually, and very small streams ceased altogether after a time. After a long search, the difficulty was located in the valves. Those we were using—the so-called "gate valves"—were found to be so constructed as to permit the accumulation of the gas, which is expelled from water when its temperature is raised, to such an extent as to impede the flow of the water, and to stop it if only a little were passing through the valves. After replacing the "gate valves" by others of the common lever variety, the trouble disappeared.

The "*heating surface*" is furnished by the two copper cylinders 9 and 10, the latter of which is broken in order to show the location of the stoves. The large wooden box is lined with

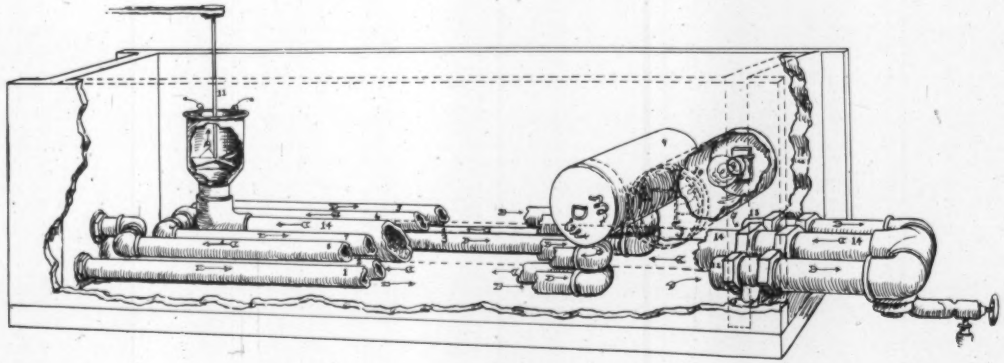


Fig. XII.

copper, and the two copper cylinders in question extend entirely through it, from side to side, and open at both ends on the outside of the bath. They are closed with caps, each of which may or may not carry a lamp. Accommodation is furnished for four lamps, but rarely more than two 32-candle power lamps are in use, even for temperatures of 50° and over. The lamps are regulated according to the scheme which was explained by means of Fig. IV.

The circulation of the water in the bath is effected by means of the pump 11. It enters the two pipes 12 and 13, and passes, in the direction of the arrows, into the large pipe 14, thence to the pump and out again into the open bath. It will be observed that the tendency is to draw the colder water upon the bottom of the bath very rapidly into the pipes 12 and 13, but that, as it enters these, it is necessarily mixed with water which has passed over the "*heated surfaces*" 9 and 10. We have tried many positions in the bath for the heated surface and have found that given in the figure the most satisfactory. The rate of pumping depends on what is found to be necessary in order to secure identical temperatures at the two ends and in the middle of the bath. Ample provision is made for any rate of pumping which may be found to be necessary. A *moderate* rate in some of the larger baths is 400 liters per minute.

The purpose in extending the pipes 12, 13 and 14 outside of the bath is obviously to economize electricity by employing gas for the major part of the heating. The rule here, as in all other baths, is to utilize the latter to the utmost safe limit, leaving for the electrical appliances only so much of the heating as is indispensible for regulation.

Five baths of type II are in use. All of them conform strictly in every particular to the plan given in Fig. XII. All have the standard arrangements for pumping and for electrical heating and regulation, also the arrangement for the circulation of hydrant water, and that for heating the water by gas. Each of the five baths is provided with all the needed accessories for experimental work with the membranes, but no attempt will be made to describe these. In-

stead, there is introduced a photograph of the baths (Fig. XIII), which will serve to give some idea of their appearance when in use.

Type III.

An example of the baths in which osmotic pressure is measured is shown in Figs. XIV and XV. The first, Fig. XIV, represents the lower part, which is filled with water, and the second, Fig. XV, the upper part, or the "air space." Both compartments are lined with copper and are separated by the vapor-tight brass plate 1, 1, which is divided diagonally across the bath into two parts, which are reunited by the brass strip 2, 2. The brass plate is screwed down upon the upper edge of the outer wooden bath, but between the two there is a strip of rubber. There is also a strip of rubber under the covering plate 2, 2. There are six lead-weighted copper cans suspended from the brass plate, and the flange of each rests upon a rubber collar. Hence, however hot the water in the bath may be, no steam ascends into the upper compartment.

It will be seen that the plan of the lower part of the bath is identical with that of the bath described under "Type II" (Fig. XII). There is in both the same system of pipes (3, 7, 8, etc.) for the circulation of hydrant water, and the same arrangement for pumping the water constantly out of the bath (through 12 and 13), to be heated by gas stoves, and returned through the large pipe—which is numbered 14. There is also in both baths the same provision for the "heated surface," the only difference being that the copper cylinders (9 and 10), in which the lamps are located, are somewhat differently placed.

The copper-lined upper part of the bath (Fig. XV) is the "air space." The electrical heating of this compartment is by means of the shaded lamps 3, 4, 5 and 6. There are two systems of pipes for the circulation of cold or hot water. One of these is located at the top of the bath 7, and is intended for hydrant water only. The other, 8, is situated at one end

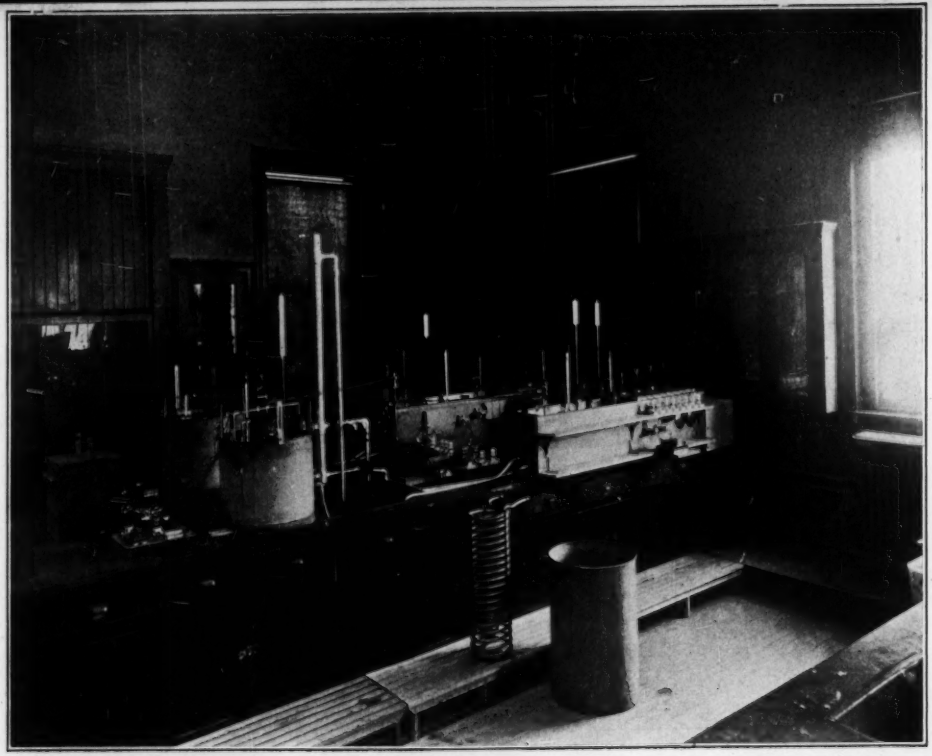


Fig. XIII.

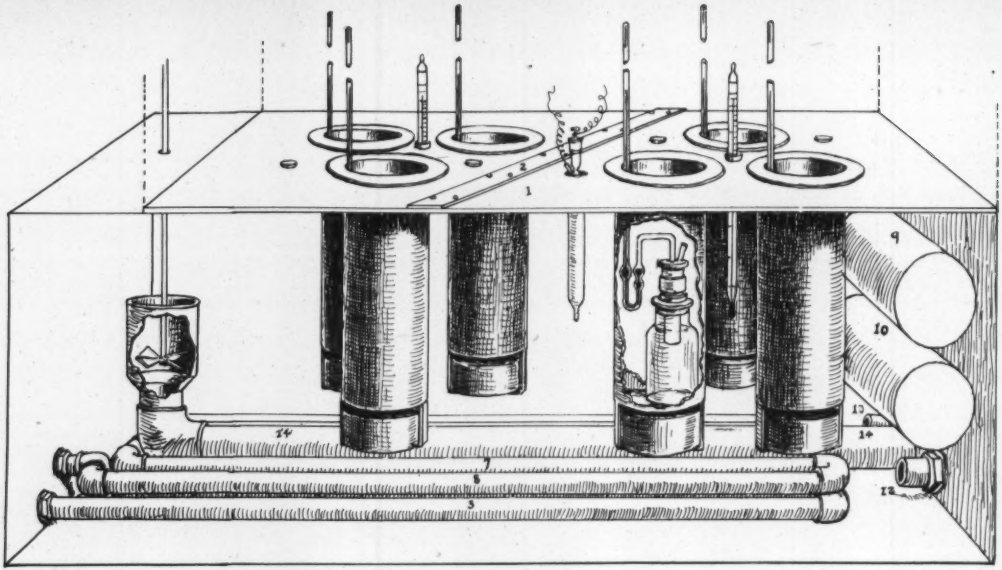


Fig. XIV.

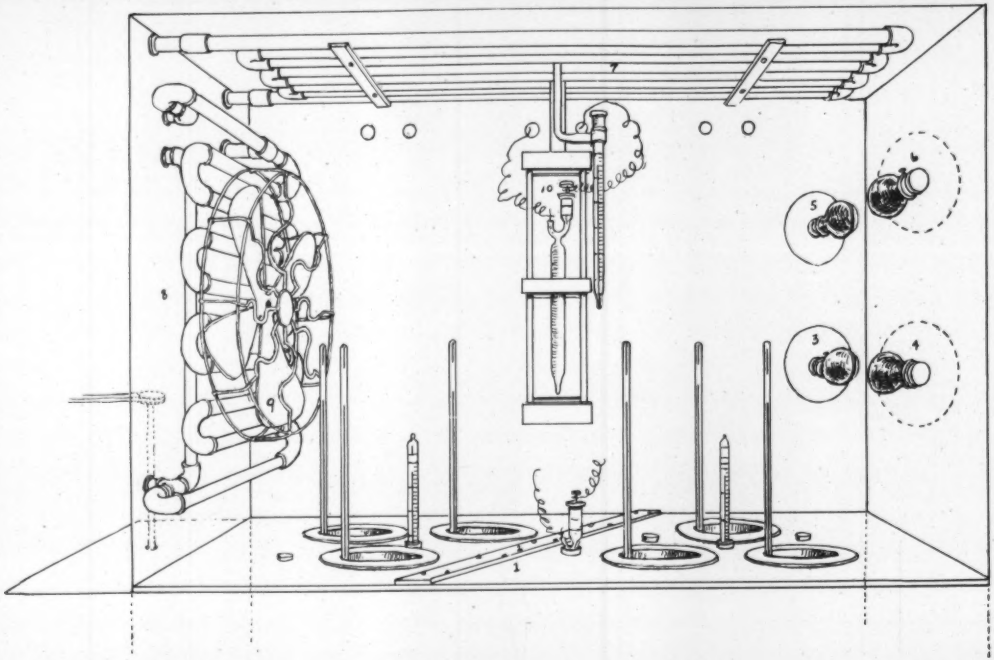


Fig. XV.

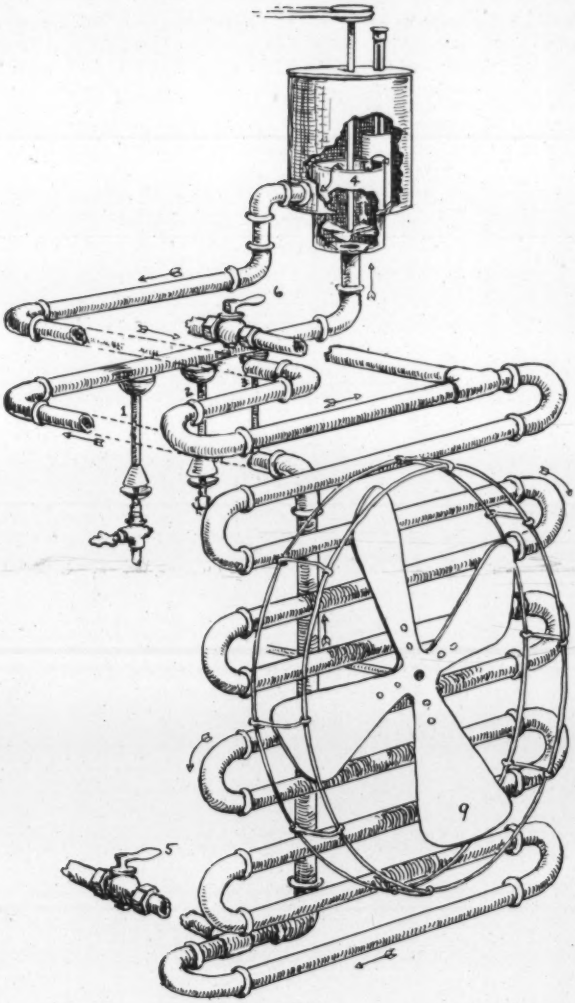


Fig. XVI.

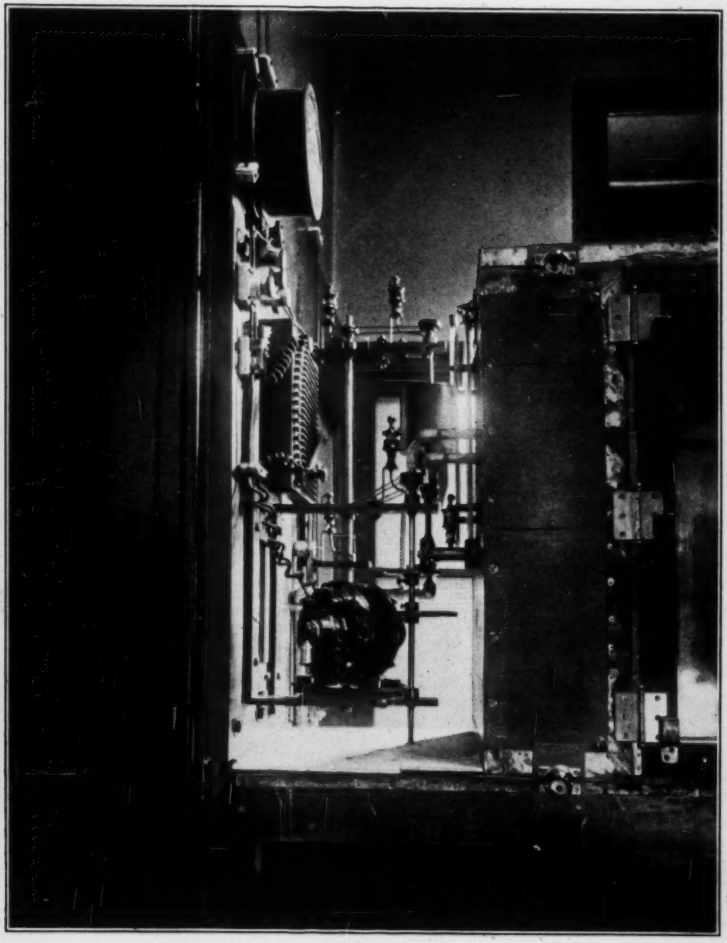


Fig. XVII.

Fig. XIII.

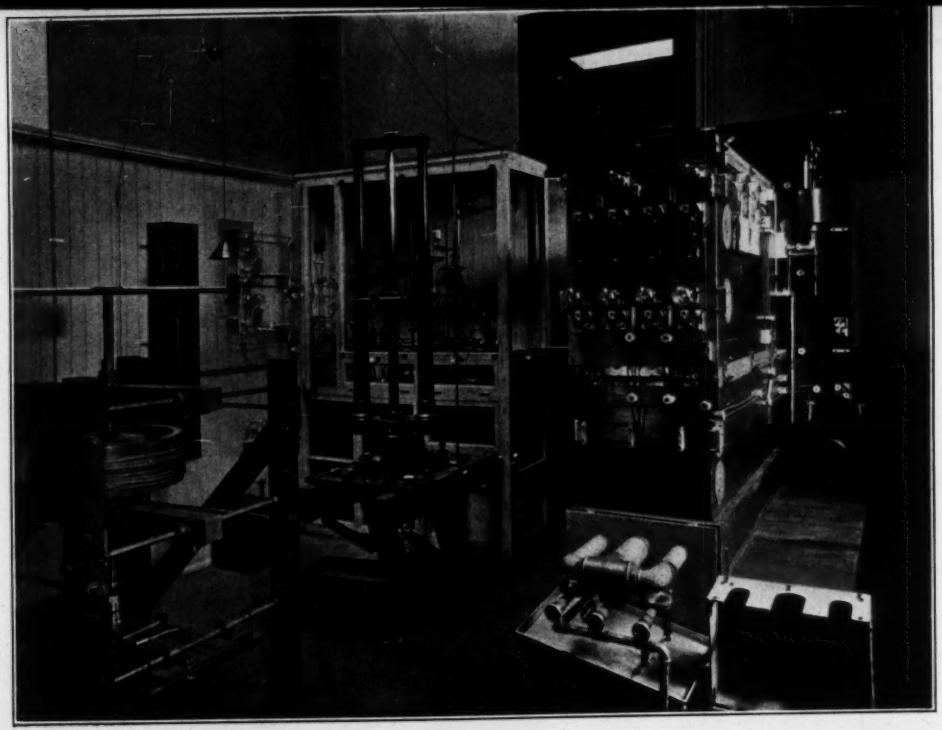


Fig. XIX.

of the bath, and is intended for either hot or cold water, but is used almost exclusively for the former.

The heating and pumping arrangements for the circulation of hot water are situated on the *outside* of the bath. Their relation to what is seen on the inside, 8, Fig. XV, is shown in Fig. XVI. The gas burners, 1, 2, and 3, heat the water on its way to the pump 4. The course of the water in the pipes is made clear by means of the arrows. When the system is used for the circulation of hydrant water, the water enters through the valve 5 and leaves through 6.

The motor fan, 9, Figs. XV and XVI, is employed to keep the air within the enclosed space in constant circulation over the heated pipes. It also serves the important purpose of keeping the manometers gently but constantly agitated, which helps to overcome the tendency of the mercury to lag in the tubes. The agitation can be increased to any desired extent by attaching bits of stiff paper to the tops of the manometers. The water in the pipes is never heated quite high enough to maintain the required temperature, a safe margin being always left to the shaded lamps at the opposite end of the bath, which are under the control of the thermostat 10.

The appearance of the outside of the bath is seen in the photographs, Figs. XVII, XVIII and XIX. Fig. XVII exhibits that portion of Fig. XVI which is exterior to the bath, also that portion of the main pump which is not seen in Fig. XIV. The opposite end of the bath, also the front and a part of the interior, are seen in Fig. XVIII. Fig. XIX gives a view of the back side of the bath and of the end at which are the arrangements for the control of the electrical heating appliances and the heating of the water in the bath by gas. Fig. XIX also includes a view of the "manometer house," and a partial view of the press for the cells.

The bath shown in the photographs is one of three which are employed for the measurement of osmotic pressure. It differs from the other two, not in principle but in that it is used for the higher temperatures. For this reason, the cold water pipes which belong in the top of the bath (7, Fig. XV) are not in position. The others, which are used mainly at

temperatures below 35°, are provided with certain accessories which are wanting in the bath seen in Figs. XVII, XVIII and XIX. They are enclosed, and the enclosures, or bath rooms, are supplied with facilities for lowering the temperature outside of the baths. One of these is an extensive system of pipes through which hydrant water can be circulated, either without or with previous cooling by means of ice. Another device, which is useful when low temperatures are required, is an arrangement for pumping outside air, at any desired rate, through the small room in which the bath is located. Formerly it was attempted to maintain the bath room as nearly as possible at the temperature of the bath, but with the present facilities for regulation, this is no longer necessary. As a rule, we now keep the temperature of the bath room about 5° below that of the bath.

JOHNS HOPKINS UNIVERSITY,
January 25, 1911.

ON THE EXPERIMENTAL ILLUSTRATION OF THE LAW OF DEFINITE PROPORTIONS THROUGH COMBINATION OF THE HALOGENS WITH FINELY-DIVIDED SILVER.

BY J. H. KASTLE.

It cannot but impress one as somewhat remarkable that, despite the great number of chemists who have, in one way or another, been engaged in the presentation of the fundamental laws of chemical combination in their relation to the atomic theory, there should have been no satisfactory method devised for illustrating experimentally the law of definite proportions. That such is the case, however, can scarcely be controverted. It may be contended, of course, that the proof of this law rests upon all chemical experience and that all known chemical processes serve to establish the truth of this generalization. For those who have a thorough knowledge of chemical science such is undoubtedly true. On the other hand, the beginner in chemistry has no experience with chemical phenomena to draw upon, especially none of quantitative relations. Hence it is that a vastly different proposition

confronts the instructor of those beginning the subject of chemistry, who finds imposed upon him the difficult task of imparting to such students a clear and clean-cut notion of the law of definite proportions in its relation to the atomic hypothesis. It has been the writer's experience that but few, if any, simple chemical changes lend themselves well to the experimental illustration of this law.

For a long time, of course, such changes as the conversion of magnesium and copper into their oxides have been employed for this purpose. Thus Tilden[1] suggests the conversion of magnesium into the oxide by heating in air and the conversion of copper into the oxide by decomposition of the nitrate. Newell[2] gives the synthesis of magnesium oxide from the elements and the decomposition of potassium chlorate as experimental illustrations of this law; and Lee[3] makes use of the synthesis of copper oxide, magnesium oxide and iron oxide. Neither of these processes, however, is free from objection. In the case of the oxidation of magnesium loss is apt to occur through volatilization of the metal, and in the case of the oxidation of the copper the direct oxidation proceeds so slowly that too much time is consumed in carrying out the experiment. The attempt has been made to remedy this by first converting the copper into the nitrate by dissolving the metal in nitric acid and decomposing the nitrate by heat. A fundamental objection to this mode of procedure is that the beginner in chemistry may fail to perceive that the black residue left after this operation contains only copper and oxygen. In other words, from the pedagogic standpoint there is a decided disadvantage in having to resort to any indirect chemical process in the experimental illustration of this law, unless the processes are such as to enable us to compare the results obtained by the simple and direct combination of the substances concerned with those reached by the more complicated method of synthesis. In other words, it is not an altogether easy matter to convince a beginner in

[1] Tilden: Hints on the Teaching of Elementary Chemistry, London and New York, 1896, pp. 13–15.

[2] Newell: Descriptive Chemistry, Boston, 1903, p. 76.

[3] A Text-Book of Experimental Chemistry, Philadelphia, pp. 43–50.

chemistry that 1 gram of copper combines with 0.25 gram of oxygen because 1 gram of the metal yields 1.25 grams of a black substance on solution in nitric acid and decomposition of the resulting compound by heat. If, however, he can also be shown that 1 gram of copper yields 1.25 grams of this same black substance as the result of heating the metal in air or oxygen, the results of the two experiments taken together tend more strongly than either of them alone to convince him that copper always combines with a definite amount of oxygen.

My own experience as a teacher of chemistry has never failed to convince me of the utter futility of attempting to teach chemical theory without suitable laboratory work on the part of the student or careful work upon the lecture table, in which instructor and student participate to as great an extent as possible. I have also never failed to be impressed with the fact that for the experimental illustration of this simplest and most fundamental law of chemical combination, viz., the law of definite proportions, we have no process at all adequate or suitable for the purpose. In this connection it has occurred to me, recently, that perhaps the combination of metallic silver with the halogens might be employed advantageously for this purpose. In its ordinary form, however, silver combines only very slowly with the halogens. Thus, according to Gautier and Charpy,[1] a silver wire lost only 0.54 per cent. of its weight after exposure to dry bromine for four months at 15°. It has recently been observed by Gooch and Perkins,[2] however, that in finely divided form silver combines quantitatively and readily with iodine, and that if the operation be carried out in an atmosphere of hydrogen, electrolytic silver may be employed in the gravimetric determinations of free iodine in aqueous and saline solutions. I have found that finely divided silver combines easily and quantitatively with chlorine, bromine and iodine under ordinary conditions and even when no special precautions are taken to exclude atmospheric air; and that these combina-

[1] Compt. rend., **113**, 597–600.
[2] Am. J. Sci., **28**, 347. Chem. News, **100**, 308.

tions lend themselves most satisfactorily to the experimental illustration of the law of definite proportions. That such is the case is evident from the following experiments. The finely divided silver employed in these experiments was prepared by the reduction of an ammoniacal solution of silver chloride by means of finely powdered cuprous chloride. When cuprous chloride is added to an ammoniacal solution of silver chloride reduction occurs at once and a finely divided grey deposit or precipitate of metallic silver is produced in a deep indigo-blue liquid. The silver thus precipitated was filtered with the aid of the pump and washed thoroughly with water until all traces of copper were removed. It was then dried in the air bath at 110° to 120° and kept in a desiccator until required for use. Thus obtained, the silver is a uniform grey powder, which in bright light shows a few particles of the glittering metal and under the low powers of the microscope is seen to consist of rounded, grey, spongelike masses, containing only a few glittering specks (probably minute crystals) of the metal. This form of silver combines with the halogens very energetically both when moist and dry. When, for example, it is brought in contact with liquid bromine it combines with it with a hissing noise and when this operation is carried out in the dark a distinct flash of light is observed.

The quantitative determinations were carried out in the following manner: Weighed amounts of the silver powder, from 0.1 to 0.2 gram, were placed in porcelain crucibles. An excess of the halogen (bromine or iodine) was then added and the crucible heated on the water bath until the excess of the halogen had been removed. The crucible was then heated to constant weight in the air bath at 120° to 150°, and then weighed. The mass of silver halide was then fused and weighed again. The increase in weight of the crucible and its contents obviously gives the weight of the halogen with which the given amount of silver has combined. In some of my experiments the silver powder was moistened with water before the addition of the halogen. So far as I have been able to observe, however, water in the liquid state in no way en-

hances the rapidity of the combination of the silver and halogen and is not essential to the process. The rapidity with which these determinations can be carried out depends, of course, on the quantities of substances started with and on the time consumed in evaporating off the excess of halogen and heating to constant weight in the air bath. In some cases, however, the entire experiment has been completed within an hour. On account of its gaseous nature chlorine has given most trouble in the quantitative determinations, for the reason that it has been difficult to bring an excess of this substance in contact with the silver in a short time. However, even with chlorine good determinations of the conversion of finely divided silver into chloride have been obtained by carrying out the reaction in a porcelain crucible. The mode of procedure is illustrated in the following determinations:

In a porcelain crucible was placed 0.1255 gram of silver powder and 5 cc. of strong chlorine water added. The crucible was then heated gently and a slow current of chlorine passed into the contents of the crucible for 15 to 30 minutes. The crucible was then heated on the water bath and its contents evaporated to dryness. It was then heated to constant weight in the air bath at 120°. The silver chloride thus obtained was found to weigh 0.1503 gram; weight of silver chloride calculated for 0.1255 gram silver, 0.1667 gram. Five cc. of strong chlorine water were then added to the contents of the crucible, which was covered with a watch glass and allowed to stand overnight at ordinary temperature. It was then placed on the water bath and its contents evaporated to dryness. The crucible was dried to constant weight in the air bath at 135°. The silver chloride now weighed 0.1666 gram. This was again treated with 5 cc. of strong chlorine water, evaporated on the water bath and heated to constant weight. The silver chloride now weighed 0.1674 gram and after fusion 0.1667 gram.

In a second experiment 0.1030 gram of silver powder were placed in a porcelain crucible and 15 cc. of strong chlorine water added. The crucible was then covered with a watch

glass and placed under a bell jar. After standing overnight the contents of the crucible were evaporated to dryness on the water bath and dried in the air bath at 130° to constant weight. The residue of silver chloride weighed 0.1367 gram; calculated for 0.1030 gram silver, 0.1368. Ten cc. of chlorine water were then added to the residue and the contents of the crucible evaporated to dryness on the water bath. Ten cc. of chlorine were again added to the residue and the contents of the the crucible evaporated to dryness and heated in the air bath to constant weight. The residue now weighed 0.1372 gram. It is possible, therefore, to convert finely divided silver completely into the chloride by a single treatment with chlorine water. It is also always possible to complete the chlorination by successive evaporations with chlorine water, even in those cases in which the first treatment with chlorine fails to convert the silver completely into the chloride. That such is the case is evident from the results of our first experiment. It is also evident from the following: 0.1003 gram of finely divided silver was exposed overnight in a covered porcelain crucible to the action of 10 cc. of the same chlorine water as that used in the preceding experiment. On evaporation to dryness and heating to constant weight the residue was found to weigh 0.1283 gram; calculated for 0.1003 gram silver, 0.1331 gram. Hence, only *85.4* per cent. of the silver had been converted into chloride. After evaporation with a second 10 cc. portion of chlorine water and drying to constant weight the residue was found to weigh 0.1305 gram (92.1 per cent. silver chloride); and after a third treatment with 10 cc. of chlorine water the residue weighed 0.1329 gram (99.4 per cent. silver chloride). After a fourth treatment with 10 cc. of chlorine water it weighed 0.1333 gram and, after fusion, 0.1329 gram.

These results suffice to show that ultimately all of the silver is converted into chloride by the action of chlorine water on the finely divided metal.

The following are the results of the syntheses of the halides of silver from the elements:

No. of experiment.	Silver taken in gram.	Silver halide obtained, in gram.	Quantity of halogen combined with silver, in gram.	Quantity of halogen which theoretically should have combined with silver taken.
1	0.1255	0.1667 AgCl	0.0412 Cl	0.0412 Cl
2	0.1003	0.1329 AgCl	0.0326 Cl	0.0328 Cl
2	0.1030	0.1367 AgCl	0.0337 Cl	0.0338 Cl
3	0.1241	0.2160 AgBr	0.0919 Br	0.0919 Br
4	0.1063	0.1847 AgBr	0.0784 Br	0.0788 Br
5	0.0360	0.0782 AgI	0.0422 I	0.0424 I
6	0.1161	0.2520 AgI	0.1359 I	0.1366 I

It is evident from these results that finely divided silver combines directly with chlorine, bromine and iodine in atomic proportions, and in view of the fact that a considerable excess of the halogen was used in all of these experiments they would serve to indicate to the thoughtful student that in every case metallic silver combines with a definite amount of halogen. By reason of the fact that we can thus synthesize the halides of silver directly from the elements it becomes possible, however, to render these results still more convincing and to put the law of definite proportions before the student, experimentally, in such a way that he cannot escape the conclusion that in the production of the halides of silver definite amounts of the elements are concerned. This is done by synthesizing the halide directly from the elements and then in several other different ways, starting in all cases with finely divided metallic silver. Thus I have prepared the chloride, bromide and iodide of silver, quantitatively, from metallic silver in three distinct ways: (1) by direct combination of the elements; (2) by solution of a known amount of metallic silver in nitric acid and evaporation with the halogen acid; and (3) by the ordinary gravimetric determination of a known amount of silver in solution in nitric acid by precipitation as the chloride, bromide or iodide with the corresponding halogen acid or metallic halide, and filtration of the silver halide on a porcelain Gooch crucible. The following are the results of these determinations:

I. Synthesis of Silver Chloride.

Method of synthesis.[1]	Ag taken in gram.	AgCl obtained, in gram.	Cl in combination with Ag, in gram.	Ratio Ag: Cl (found).	Ratio Ag: Cl (calc. from at. wts.).
(*1*)	0.1255	0.1667	0.0412	1 : 0.3283	1 : 0.3287
(*2*)	0.1255	0.1668	0.0413	1 : 0.3290	
(*3*)	0.1080	0.1433	0.0353	1 : 0.3268	

II. Synthesis of Silver Bromide.

Method of synthesis.	Ag taken, in gram.	AgBr obtained, in gram.	Br in combination with Ag, in gram.	Ratio Ag: Br (found).	Ratio Ag: Br (calc. from atomic wts.).
(*1*)	0.1241	0.2160	0.0919	1 : 0.7405	1 : 0.7408
(*2*)	0.1087	0.1890	0.0803	1 : 0.7397	
(*3*)	0.1066	0.1851	0.0785	1 : 0.7364	

III. Synthesis of Silver Iodide.

Method of synthesis.	Ag taken in gram.	AgI obtained, in gram.	I in combination with Ag in gram.	Ratio Ag: I (found).	Ratio Ag: I (calc. from atomic wts.).
(*1*)	0.0360	0.0782	0.422	1 : 1.1722	1 : 1.1765
(*2*)	0.1003	0.2180	0.1177	1 : 1.1735	
(*3a*)	0.1033	0.2242	0.1209	1 : 1.1704	
(*3b*)	0.1043	0.2263	0.1220	1 : 1.1697	

Reducing these numbers to two places of decimals, it is evident from the above results that under three distinctly different sets of conditions 1 gram of silver combines with 0.33 gram of chlorine, with 0.74 gram of bromine and with 1.17 grams of iodine. It is only logical to conclude, therefore, that silver always combines with definite masses of the halogens, no matter how the combination may be brought about.

UNIVERSITY OF VIRGINIA,
November, 1910.

OBITUARIES.

JACOBUS HENRICUS VAN'T HOFF.

It is with no ordinary feeling of sorrow that we learn of the death of van't Hoff. With him there has passed away one

[1] In the above table in the syntheses marked (*1*) the halides were made from the elements. In those marked (*2*) they were made by dissolving the silver in nitric acid, adding an excess of the halogen acid and evaporating to dryness in a porcelain crucible. In those marked (*3*) they were made by the usual method of precipitating a known amount of silver dissolved in nitric acid with a metallic halide or halogen acid. In (*3*) under the synthesis of silver chloride, sodium chloride was used; in (*3*) under silver bromide, potassium bromide; in (*3a*) under silver iodide, potassium iodide; and in (*3b*), hydriodic acid.

of the greatest men of science not only of his age, but of all time—a man who found chemistry in a certain state of development, and who left it incomparably more nearly an exact branch of natural science—and these advances were due, directly or indirectly, primarily to the work of van't Hoff.

It is not the intention to give, in this brief notice, a biographical sketch of van't Hoff but to deal mainly with his work. Yet a few matters pertaining to his life should be mentioned. Born in Rotterdam, August 30, 1852, and passing away in Berlin on March 1, 1911, he was in his fifty-ninth year. He was the son of a physician, was trained in the Realschule in Rotterdam, and in the Polytechnicum in Delft, and completed his work at the University of Leiden at the age of twenty. He continued his studies at Bonn under Kekulé, and at Paris under Würtz, and at the age of twenty-two obtained the Doctor's degree at the University of Utrecht. In 1876 he became Privatdozent in physics in the veterinary college in Utrecht. In 1877, he was called to Amsterdam as lecturer in chemistry. In 1878 he became professor of chemistry in the University of Amsterdam, a position which he filled until 1894, when he was called to the University of Berlin, where he remained until his death.

van't Hoff will go down in the history of science primarily as having done three things:

(1) Having founded the science of stereochemistry.

(2) Having applied the law of mass action to chemical reactions, and thus opening up the fields of chemical dynamics and chemical equilibrium.

(3) Having pointed out the close relations between solutions and gases, and thus placing solutions upon a scientific basis.

Let us look more closely into the origin and nature of each of these epoch-making contributions to chemistry.

At the age of twenty-two, when a pupil of Mulder in Utrecht, van't Hoff published, in Dutch, a paper, eleven pages in length, which, he said to the writer only a year and a half ago, gave him as much pleasure to look back upon as any publication that he had ever made.

This paper had to do with the great and, up to that time, apparently hopeless problem of "structural formulae in space." In the following year this was translated into French under the title "La Chimie dans l'Espace."

Wislicenus, two years later, wrote the preface to the translation of this paper into German and saw in it the dawn of a new day for organic chemistry.

From the work of Henri and others, which showed that methane is a symmetrical compound, van't Hoff pointed out that we are forced of mathematical necessity to conclude that methane must be represented in space by the symmetrical tetrahedron, the carbon atom being situated at the center of the tetrahedron and the four hydrogen atoms at the solid angles.

Pasteur had been studying the property possessed by certain substances of rotating the beam of polarized light, and had concluded that in order that a compound should be optically active it must possess some kind of asymmetry. He, however, was unable to point out the kind of asymmetry represented in the molecule. This remained for van't Hoff. He simply extended his theory of the "tetrahedral carbon atom" to that of the "asymmetric tetrahedral carbon atom" or a carbon atom in combination with four different atoms or groups, and the phenomena of optical activity were explained. An examination of all the optically active compounds of carbon then known showed that they all contain at least one carbon atom in combination with four different things, and the same applies to all of the hundreds of optically active compounds of carbon known to-day. Even the terpene derivative which, for a time, was supposed by Baeyer to have no asymmetric carbon atom and which is optically active, has since been shown to contain an asymmetric carbon atom.

This was the beginning of the stereochemistry of carbon, which has led to such brilliant results in the hands of Wislicenus, Baeyer, Hantzsch, Wollach, Fischer and others. Indeed, it is hardly too much to say that stereochemistry has been the philosophy of organic chemistry for the past quarter of a century.

One result of van't Hoff's work with Kekulé and of his study of organic compounds was the writing of his book "Ansichten über die organische Chemie," which he says was written with the view of clearing up his own ideas on the subject. Another result of the influence of Kekulé on van't Hoff and of the latter's interest in organic chemistry was the founding of the science of chemical dynamics and chemical equilibrium.

van't Hoff was impressed with the purely qualitative nature of organic chemistry in that day. Certain substances were brought together under certain conditions, and certain products were formed in determinable quantities—certain "yields" obtained. Little or nothing, however, was done to ascertain quantitatively the velocity with which the reaction in question takes place, the nature of the intermediate products formed, or the conditions when equilibrium is reached. While

Guldberg and Waage were the discoverers of the law of mass action, and applied it to the dynamics of a few chemical reactions, it was van't Hoff who first showed its general applicability to the dynamics and equilibrium of reactions in which compounds of carbon are involved. While these matters were touched upon in his "Ansichten über die organische Chemie," the results of the experimental work of himself, assistants and students, together with their theoretical discussion, were first published in 1884 in his "Etudes de Dynamique Chimique."

In reference to this work Ostwald[1] says: "Hier ist es, wo die Bemühungen unseres Forschers einsetzen, und es ist nichts weniger, als das ganze Gebiet der chemischen Dynamik, die Lehre von der Geschwindigkeit wie die vom chemischen Gleichgewicht, deren systematischen Aufbau er unternimmt. . . . Der Ansatz der Grundgleichungen für die Kinetik und das Gleichgewicht erfolgt wesentlich auf dem Boden der Molekularhypothese, und es werden die mono-, di- und trimolekularen Reaktionen unterschieden. Dies geschieht im Gegensatz zu den älteren Formulierungen von Guldberg und Waage, bei denen bloss die wirksamen Mengen in Reaktionsäquivalenten in Rechnung gezogen worden waren. Die Entwickelung der Wissenschaft hat unserem Forscher hierin wesentlich recht gegeben, und die von van't Hoff selbst nach dem Vorgange Horstmanns durchgeführte Anwendung der Energetik auf dieses Problem hat der ursprünglichen auf der Molekularhypothese beruhenden Begründung die zur Zeit sicherste Stütze gewährt. . .

"In der Anwendung der Thermodynamik auf die chemischen Probleme bewährt er alsbald die Meisterhand. Als Zeichen für die Weite seines Blickes und seine Fähigkeit, das Wesentliche in der Fülle der Erscheinungen zu sehen, sollen nur die Formulierung der Beziehung zwischen chemischem Gleichgewicht und elektromotorischer Kraft, sowie sein berühmtes Prinzip des beweglichen Gleichgewichts genannt werden, welches die Beziehung zwischen der Aenderung der Bedingungen eines Gebildes und der Beschaffenheit der Vorgänge ausspricht, die durch diese Aenderungen im Gebilde hervorgerufen werden.

"Die Wirkung des Buches war eine ähnliche, wie die seiner stereochemischen Ansichten: sie erfolgte nicht schnell, war aber um so tiefgreifender. Immer wieder wird die Forschung auch noch heute auf die Gedanken zurückgelenkt, die sich dort entwickelt finden, und der Umfang des Einflusses, den es

[1] Z. physik. Chem., **31**, xiii (1899).

auf die Zeit und Arbeitsgenossen geübt hat, lässt sich auch nicht annähernd abschätzen."

This brings us to the third great epoch-making contribution of van't Hoff to chemistry in particular, and science in general; the relation between solution and gases, which is regarded by many physical chemists as his most important work. It is interesting to learn how van't Hoff came upon this problem, and especially interesting to learn it in his own language. In his celebrated Berlin lecture of 1894 before the German Chemical Society, and which led directly to his call to the University of Berlin, he tells the story.[1]

"Jung wie ich war, wollte ich dann auch die Beziehungen zwischen Constitution und chemischen Eigenschaften kennen lernen. Die Constitutionsformel soll ja doch schliesslich Ausdruck des ganzen chemischen Verhaltens sein.

"So entstanden meine 'Ansichten über die organische Chemie,' die Sie wohl nicht kennen. Es lohnt sich auch kaum. Nur hatten sie für mich den Werth, dass sie eine bestehende Lücke mir sehr scharf zeigten.

"Nehmen wir ein Beispiel!

"Wie bekannt, übt in organischen Verbindungen der Sauerstoff eine beschleunigende Wirkung auf fast sämmtliche Umwandlungen aus: Oxydation bei CH_4 schwerer als bei CH_3OH u. s. w.

"Um jedoch daraus werthvolle Beziehungen zu erhalten, ist genaue Kenntniss der Reactionsgeschwindigkeit Bedürfniss, und so gings zur Reactionsgeschwindigkeit, und es entstanden meine:

Etudes de dynamique chimique.

"Reactionsgeschwindigkeit zunächst als Hauptzweck. Chemisches Gleichgewicht aber unmittelbar daneben. Wo doch das Gleichgewicht einerseits auf Gleichheit zweier entgegengesetzter Reactionen beruht, und andererseits durch seine Verknüpfung mit der Thermodynamik eine feste Stütze gewährt.

"Sie sehen, um mein Ziel zu erreichen, kam ich stets weiter vom Ziel; das kommt öfter vor.

"Und weiter musste ich noch, denn die Gleichgewichtsfrage grenzt unmittelbar an das Affinitätsproblem, und so war ich angelangt bei der sehr einfachen Affinitätserscheinung, zunächst derjenigen, welche als Wasseranziehung sich äussert.

"Schon Mitscherlich hatte sich in seinem Lehrbuch der Chemie[2] die Frage gestellt nach der Grösse der Anziehung,

[1] Ber. d. chem. Ges., **27**, 7 (1899).

[2] 4. Auflage, 565 (1844).

welche das Krystallwasser im Glaubersalz zurückhält.' Ein Maass dafür erblickte er in der verminderten Krystallwassertension:

"'Wenn man in die Barometerleere bei 9° Glaubersalz bringt, sinkt das Quecksilber um 2.5 Linien (5.45 mm.) durch Wasserdampfabgabe. Wasser selbst bewirkt dagegen eine Senkung von 4 Linien (8.72 mm.)—die Affinität des Natriumsulfats zu seinem Krystallwasser entspricht also der Differenz 1.5 Linien (3.27 mm.) d. i. etwa 1/16 Pfd. (1/32 kg.) pro Quadratzoll (2.615 qcm.).'

"Dieser Werth, 1/200 Atm., kam mir unerhört klein, hatte ich doch den Eindruck, dass auch die schwächsten chemischen Kräfte sehr gross sind, wie es mir z. B. auch aus Helmholtz' Faraday Lecture hervorzugehen schien.

"So lag die Frage nahe, ob nicht noch in einfacheren Fällen diese Wasseranziehung in mehr directer Weise zu messen sei, und dann ist wohl die wässrige Lösung die einfachst denkbare, bedeutend einfacher als die Krystallwasserbindung.

"Mit dieser Frage auf den Lippen aus dem Laboratorium kommend, begegnete ich dann meinem Collegen de Vries und seiner Frau; der war gerade mit osmotischen Versuchen beschäftigt und machte mich mit Pfeffer's Bestimmungen bekannt."

This was the introduction of van't Hoff to the osmotic work of Pfeffer, and we all know more or less of the result. With that insight into the real meaning of phenomena, and that foresight that enables one to see relations from very meager and imperfect data, which are characteristic of the highest genius, van't Hoff saw from the few osmotic pressure measurements of Pfeffer the relations between solutions and gases—the laws of gas pressure applied to the osmotic pressure of solutions. In a word, we could deal with solutions as with gases.

The importance of this relation is obvious to any one. We know comparatively little of matter in the solid state, very little more than the forms in which it crystallizes, and the way in which it conducts certain forms of energy. We know more of matter in the liquid state, but even here our knowledge is far from satisfactory. When, on the other hand, we come to gases our knowledge is much more satisfactory. We know a great deal about matter in this most dilute condition, and can deal with gases satisfactorily from the thermodynamic standpoint.

When van't Hoff showed that we can deal with solutions by the same rigid methods that we employ with gases, he made a contribution not only to chemistry, but to science in

general, the importance of which it is difficult to overestimate. A moment's thought will show how this is true. The whole subject of chemistry is primarily a science of solutions in the broader sense of that term. The same applies to geology, by solutions being meant not only solutions in water but in molten magmas as well. The subject of solutions is fundamental to practically every one of the biological sciences, experimental morphology, experimental botany, physiology, pharmacology, physiological chemistry, pathology, bacteriology, etc., and solutions play an important rôle in many branches of physics, especially in connection with the action of the primary cell.

It is obvious that any suggestion which would place the subject of solutions upon a scientific basis, and especially upon an exact basis, would be of fundamental importance not only for chemistry, but for all the natural sciences, and such was the relation between solutions and gases pointed out by van't Hoff.

van't Hoff not only showed the applicability of the gas laws to the osmotic pressure of solutions of nonelectrolytes, but he saw clearly the exceptions to these relations presented by electrolytes. In his great paper in the first volume of the *Zeitschrift für physikalische Chemie*, in which the above relations were formulated, he pointed out with equal clearness the exceptions presented by electrolytes—exceptions which a little later, in the hands of Arrhenius, led to the theory of electrolytic dissociation, another cornerstone in the structure of chemical science.

This was the third great contribution of van't Hoff to science, and from its wide-reaching significance is, in the opinion of the writer, the most important of them all.

We speak of van't Hoff having made three great contributions to chemistry in particular and to science in general. This is only by comparison. He opened up other fields which are only less important than the three in question and which would have made any less prominent man famous.

Take, for example, his paper on "Feste Lösungen."[1] Before this paper appeared we either never heard of the subject of solid solutions, or heard of it in a very casual way. In this paper van't Hoff pointed out that certain mixtures of solids have all the properties characteristic of solutions of solids or liquids in liquids—have all the properties of solutions in liquids as the solvent. Since the appearance of this paper, we have dealt with solid solutions as distinctively and almost as concretely as with liquid solutions; and in the hands of Ciamician and his coworkers, and of Küster, important developments have resulted.

[1] Z. physik. Chem., **5**, 322 (1890).

The most recent experimental work of van't Hoff in connection with the tremendously complex problems presented by the various salt beds deposited from desiccated inland seas, has geological interest: but this work is not in the same class with that discussed above.

This sketch of the work of van't Hoff would be unnecessarily imperfect and unsatisfactory were not something said in reference to the personality of this great man.

The writer had the good fortune to know van't Hoff in the relation of student to teacher for a short time in the spring of 1894.

My chief object in going to his laboratory was to learn, if possible, the methods by which he worked. When dealing with any problem, he would collect all of the reasonably reliable data bearing upon that problem, bring it together and study it.

The question has often come up whether van't Hoff was a great experimenter. This is a matter of very little consequence. He did not need to experiment. There are plenty of others to do that. He was primarily an interpreter of the experimental results obtained by others, and he interpreted these results in such a way as to revolutionize chemistry.

During the short period that I was in his laboratory in Amsterdam, he worked continually and very intensely in his laboratory, but the results of that work were never published, and this is the key to the difference of opinion that prevails in reference to van't Hoff the experimenter. He did not publish the results that he obtained simply for their own sake. If they bore on some theory or generalization in which he was interested they were published. If not, or if their meaning was not clear, they never saw the light. He seemed to look upon his own experimental work as valuable, not in itself, but only as it proved or disproved some idea that he had in mind. Consequently, a large amount of the work that he did in the laboratory with his own hands was never published.

During the Amsterdam period van't Hoff impressed me as one who was living under an intense nervous and mental strain. His walk, his speech, and the characteristic nervous twitch of the eye all pointed in this direction. For power of concentration and intensity, I know of only one other who could be compared with him, and that was Rowland.

After going to Berlin van't Hoff seemed to have lost some of his earlier intensity, probably due to the progress of the horrible malady which brought such an untimely end.

When I saw him last, a year and a half ago, although he was suffering very severely, the same personal characteristics

that marked his earlier life were still there. An unusual modesty, a dislike for all show and ostentation, a simple, frank, open, honest, unselfish nature were a few of the attributes that must have impressed themselves upon all who knew him.

van't Hoff enjoyed what is not given to all great men. He lived to see his work fully recognized and appreciated. He was elected a member of most of the learned societies and academies of the world, and was awarded the first Nobel prize in chemistry, which shows how he was valued by the leading chemists of his day.

Although it always requires time to fix the exact position of any great man, yet we are certainly justified in placing van't Hoff in the very first rank of such men as Dalton, who gave us the laws of definite and multiple proportions; Avogadro, whose hypothesis has done so much for chemistry; Berzelius, the father of analytical chemistry; Lavoisier, who told us what combustion really is; Liebig, who transplanted chemistry from France to Germany; Wöhler, who coöperated with Liebig in his most important work; Kekulé, who gave a new impulse to organic chemistry; Hofmann, Baeyer and Victor Meyer, who took up organic chemistry where Liebig, Wöhler and Kekulé left it, and showed us its real meaning for science as well as for the material good of the human race; Fischer, who, influenced by the stereochemical conceptions of van't Hoff, made organic chemistry what it is to-day; Ramsay, who not only discovered the rare gases in the atmosphere and in the earth, but who showed us the birth of a new element; Arrhenius, who has furnished chemistry with one of the greatest generalizations of all times; Ostwald, who contributed so much experimentally to the development of modern physical chemistry, and who brought order and system into the entire science of physical chemistry, not to say of chemistry in general.

Without presuming to compare van't Hoff with these other great men, his work stands out not simply for the *importance* of the generalizations which he reached, but for their *number*.

The question that men of science will ask is, When shall we have his like again?

HARRY C. JONES.

LEONARD PARKER KINNICUTT.

The death of Prof. Leonard Parker Kinnicutt, well known through his contributions to sanitary chemistry and a recognized expert on sewage disposal and water supply, was announced February 6th. Prof. Kinnicutt was born at Worcester, Mass., May 22nd, 1854. His early training was received at the Massachusetts Institute of Technology, where he ob-

tained the degree of B.S. in 1875. He studied four years at Heidelberg and Bonn and one year at the Johns Hopkins University, and in 1882 made his D.Sc. at Harvard, where he had been instructor in quantitative analysis since 1880. The following year he was appointed assistant professor of chemistry at the Worcester Polytechnic Institute and remained at that institution till the day of his death, being promoted to a full professorship in 1886 and made director of his department in 1892. He took an active interest in questions of public health and for the last eight years served as consulting chemist to the Connecticut Sewerage Commission. He was a member of many scientific societies. His main contributions to science and the public welfare have dealt with sewage disposal; sanitary problems in connection with air and water; quantitative methods of determining carbon monoxide; standard methods in the analysis of potable waters and sewage; septic tank and intermittent filtration methods for the treatment of sewage.

REVIEWS.

A TEXT BOOK OF ORGANIC CHEMISTRY. By WILLIAM A. NOYES, Professor of Chemistry in the University of Illinois. Second edition, revised. New York: Henry Holt and Company. 1910. pp. xvii + 537.

In regard to this edition the author says, "The chapter on Compounds of Interest in Physiology and Pathology has been rewritten on the basis of the classification of proteins recently adopted by the American Society of Biological Chemists and the American Physiological Society." He further says: "A number of other changes and additions, most of which were prepared for the German edition of this book, have also been included." When the first edition appeared the book was noticed in THIS JOURNAL[1] and reference may here be made to what was then written in regard to it. The fact that a second edition is called for is further evidence that the author's method of presentation has found favor with a fair number of scholars. It is further interesting to note that the book has been translated into German and that no less a chemical light than Ostwald has written an Introduction to the German edition. The author is to be congratulated upon the success of his book.

[1] THIS JOURNAL, **31**, 85.

GRUNDLAGEN UND ERGEBNISSE DER PFLANZENCHEMIE. Nach der schwedischen Ausgabe bearbeitet von H. EULER, Professor der Chemie an der Universität Stockholm. Zweiter Teil: Die allgemeinen Gesetze des Pflanzenlebens. Dritter Teil: Die chemischen Vorgänge im Pflanzenkörper. Braunschweig: Friedrich Vieweg und Sohn. 1909. s. viii + 298. Prices, geh., M. 7; geb., M. 8.

This volume, which embodies the second and third parts of the work on "Pflanzenchemie" now completed by our brilliant and versatile colleague, is even more attractive than the first one.

In a very entertaining introduction Euler shows the debt which botanists, especially the newer school of plant physiologists, owe to organic and physical chemistry.

In the second part he takes up the general laws of plant life and discusses in detail, with full references, the importance to the plant chemist of osmotic pressure, the mass law, electrolytic dissociation, solubility, colloids, reaction velocities, the plant enzymes (including hydrolytic enzymes, fermentative enzymes, oxidases and catalases), the influence of temperature and light on chemical reactions, and optical activity.

In the third part the chemical processes of the plant life are discussed in the sections on the assimilation of carbon, nitrogen, and minerals, and on respiration, fermentation, and the synthesis of proteids, carbohydrates, and fats. The end products of the synthetic processes and their relation to plant growth and the development of the individual organs are fully treated. There is finally an interesting chapter on the origin of organic compounds, life phenomena, and organized entities.

All chemists and botanists will find much pleasant and instructive reading in this book.

S. F. ACREE.

ANALYTICAL CHEMISTRY. Volume II. Quantitative Analysis. By F. P. TREADWELL, PhD., Professor of Chemistry in the Polytechnic Institute of Zurich. Authorized Translation from the German by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Second Edition. Thoroughly revised and enlarged. New York: John Wiley & Sons. London: Chapman and Hall, Limited. 1910. pp. x + 787.

The number of authoritative works dealing with general analytical procedures, and of such scope as to be useful alike for practitioner and student, is not large to-day and it is fortunate that the author and translator of this well-recognized hand-book are so painstaking in its revision. The present edition merits the same favorable comments as its predecessor. This, the second edition, is translated from the

fourth German edition, and the translator has added a number of procedures which have found favor among American chemists, but have not as yet been incorporated in the German edition. Among the latter are Blasdale's separation of calcium and magnesium, the determination of nickel as glyoxime, and that of zinc as zinc ammonium phosphate, the determination of nickel in steel (Brünck), a procedure for the analysis of bronzes, the determination of vanadium, molybdenum, chromium, and nickel in steel, the Bamber method for sulphur in iron or steel, some modifications of the procedure for carbon in steels, the Brown method for silicon, the bismuthate and Williams method for manganese, the Blair rapid method for phosphorus, the iodate method for copper, the cyanide titration for nickel, the Low method for copper, and the use of rotating electrodes for a number of determinations. The procedures thus added are generally recognized as useful and reliable, and the details as given are, in nearly all cases, those found desirable by the translator on the basis of his instructional experience and private analytical practice. The volume can be heartily commended to the attention of all analysts and teachers. H. P. TALBOT.

A COURSE OF QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES, with Explanatory Notes. By OLIN FREEMAN TOWER, Ph.D., Hurlburt Professor of Chemistry in Adelbert College of Western Reserve University. Philadelphia. P. Blakiston's Sons & Co. 1909. pp. xi + 83.

Professor Tower's book is written from a physical-chemical standpoint; its great advantage is its conciseness and clearness. The introduction is only 14 pages in length, but it is an admirably clear explanation of the application of modern ideas to analysis. Few equations are given and there are no tables. The author employs the method of Noyes and Bray for separating antimony from tin, the basic acetate method for the iron group, and separates strontium from calcium by amyl alcohol.

In the reviewer's opinion this is one of our best laboratory manuals for college work. E. R.

QUALITATIVE CHEMICAL ANALYSIS FROM THE STANDPOINT OF SOLUBILITIES, IONIZATION AND MASS ACTIONS. By J. I. D. HINDS, Ph.D., LL.D., Professor of Chemistry, University of Nashville and Peabody College for Teachers, Nashville, Tennessee. Easton, Pa.: Chemical Publishing Company. 1910. pp. vii + 266. Price, $2.00.

The ground covered in this book is the same as in the average college manual. The theoretical part is clear, the older standard methods are generally retained, but the author

introduces the Benedict method for the separation of cobalt and nickel. The properties and reactions of the elements are given with unusual fullness. Fifty pages are given to principles and methods and over 200 pages to properties, reactions and analysis.

The great length of the book compared with the ground covered, the printing of all the equations in full instead of allowing the student to work them out for himself, and the use of tables may all be criticized. The book is carefully compiled however, and merits examination. E. R.

TRAITÉ COMPLET D'ANALYSE CHIMIQUE APPLIQUÉE AUX ESSAIS INDUSTRIELS. PAR J. POST, Professeur Honoraire à l'Université de Goettingue, et B. NEUMANN, Professor à la Technische Hochschule de Darmstadt. Avec la collaboration de nombreux chimistes et spécialistes. Deuxième édition française traduite d'après la troisième édition allemande et augmentée de nombreuses additions par G. CHENU, Ing. E. P. C., et M. PELLET, Ing. I. N. A. Tome second. Troisième fascicule. Paris: Librarie scientifique A. Hermann et Fils. 1910. pp. 418. Price, Fr. 13.

This portion of Post's Technical Analysis comprises the examination of beer, wine, cider and perry, alcohol, compressed yeast, vinegar and wood alcohol. The methods given are for the most part the customary ones established by general usage. The results of the latest researches are not always incorporated and the reader will look in vain for several processes which have been shown by recent work to possess distinct advantages over those formerly in use. Conservatism in this respect, however, is hardly to be regarded as a defect in a book intended as a standard work in a broad field. Much space is devoted to the official German and French methods. As a compilation of standard methods of these countries the book is distinctly useful. A. G. WOODMAN.

ENGINEERING CHEMISTRY. A Manual of Quantitative Analysis for the Use of Students, Chemists and Engineers. BY THOMAS B. STILLMAN, M.Sc., Ph.D., Late Professor of Engineering Chemistry in the Stevens Institute of Technology. With 174 Illustrations. Fourth edition. Easton, Pa.: Chemical Publishing Co. 1910. pp. ix + 744. Price, $5.

The fourth edition of this widely used work contains all the valuable features of its predecessors, with considerable amplification of some of the sections. Most notable of these additions occur in the chapters on Fuels, Boiler Waters, Pyrometry, Lubricating Oils, and Paints. The contributed articles on Foundry Chemistry, Official Methods of Sampling Iron Ores, and Acetylene are new.

As a whole, this treatise fills a well-defined need of the prac-

tical chemist and engineer; in the principal branches of technology it furnishes methods for the analysis of raw materials and products, in some cases notes on the processes themselves and on control of the same, and in many others methods of physical testing and good recent specifications for the guidance of manufacturers and buyers. The best of these are probably the sections on Fuels, Water, Portland Cement, Paper, Soap, and Lubricating Oils. In addition there are numerous valuable tables, while throughout the book are given copious references to original sources and to extended treatments of the various subjects. As a ready, suggestive reference book it is therefore warmly commended to practitioners and students. There are, however, features open to criticism.

The arrangement and distribution of space are poor. The chapter on Alloys is desultory, and comes between those on Paper and Gelatin Dynamite, while Pyrometry is treated near the end of the book. There are thirteen pages devoted to the causes of saline efflorescence in bricks, but only two to the technology of rubber. Seven viscosimeters are described and illustrated, while only the Berthelot type of calorimeter is treated. This haphazard method extends alike to the internal material of the various chapters. Portland cement receives good treatment from many angles, while steel is dismissed with short methods for chemical analysis, some unreliable remarks on its microstructure, and a general classification of its grades. There are too many pages of unedited contributions and not enough of well-digested authoritative matter.

The methods for analysis given are generally of the rough and ready type, giving quick results, of doubtful accuracy. Realizing the technical demand for speed, we would not eliminate these methods entirely, but suggest the insertion of alternate procedures for the benefit of those desiring a higher degree of accuracy. Careful editing and revision would double the value of this work, which now impresses the reader as a voluminous note book.

K. W. ZIMMERSCHIED.